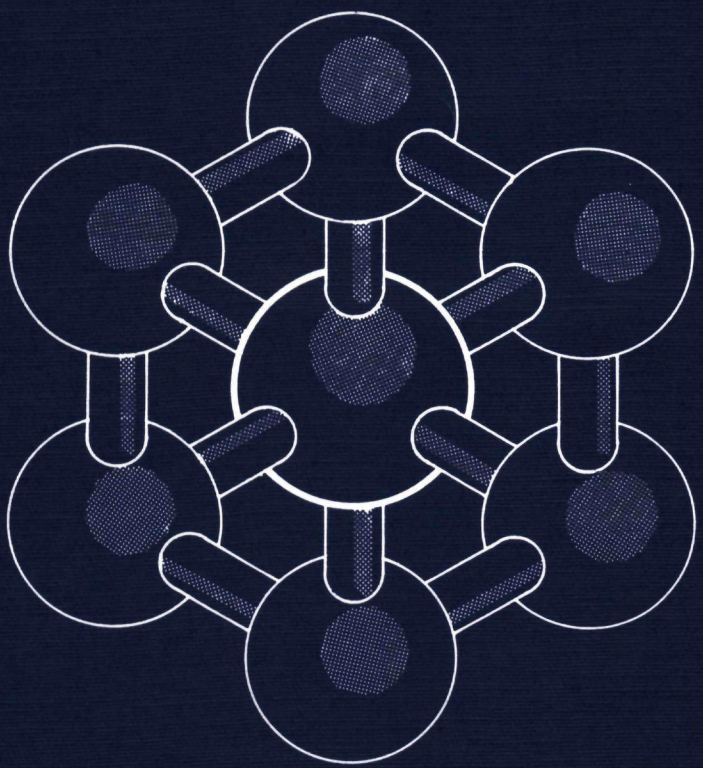
# HIGH RESOLUTION MEASUREMENTS OF MULTIPHOTON MULTI LASER EXCITATION OF $SF_6$



SACCO TE LINTEL HEKKERT

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EEN WETENSCHAPPELIJKE PROEVE OP HET GEBIED VAN
DE NATUURWETENSCHAPPEN

## PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
AAN DE KATHOLIEKE UNIVERSITEIT NIJMEGEN,
VOLGENS BESLUIT VAN HET COLLEGE VAN DECANEN
IN HET OPENBAAR TE VERDEDIGEN
OP DONDERDAG 4 FEBRUARI 1993,
DES NAMIDDAGS TE 3.30 UUR PRECIES

door

**SACCO TE LINTEL HEKKERT**

geboren op 11 maart 1963
te Deventer

Promotor : Prof. Dr. J. Reuss

**Een woord van dank**

De laatste zes jaar heb ik een groot deel van mijn tijd op de afdeling Molecuul- en laserfysica doorgebracht, met veel genoegen kijk ik terug op deze periode Van deze gelegenheid wil ik dan ook gebruik maken om iedereen te bedanken die op enigerlei wijze een bijdrage heeft geleverd aan het totstandkomen van dit proefschrift Enkelen van hen wil ik met naam noemen

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-En natuurlijk het F.O.M. (stichting fundamenteel onderzoek der materie) zonder wiens geldelijke ondersteuning dit onderzoek niet gedaan had kunnen worden.

# Contents

# Chapter 1

# General introduction

The research on $SF_6$ started in 1934 when the first measured Raman and infrared spectra were published [1] At the same time theoretical considerations of the normal modes in $SF_6$ were published [2] The discovery of infrared Multiphoton excitation (MPE) and multiphoton dissociation (MPD) in 1973 [3, 4] created much interest and projects were initiated where laser induced processes and new concepts like the quasicontinuum of states and the leakage of energy to dark bath-states played an important role In many studies detailed aspects of these phenomena were elucidated, for review see [5] MPD was observed in a molecular beam in 1979 by Yuan Lee and coworkers demonstrating above any doubt the collisionless character of MPE and MPD [6] The somewhat deluding conclusion was forced upon the scientists that in dissociation always the weakest bond was ruptured and that a steering of the process by appropriate laser wave lengths and intensities was more difficult than expected [7]

To investigate the first steps in the MPE process, McDowell et al [8] and Patterson et al [9] refined the theory of one, two and three photon transitions Overtone measurements of $3\nu_3$ transitions in $SF_6$ were published in [10] where a spectral resolution of 30 MHz is achieved

$SF_6$ measurements with resolutions in the kHz region for the one photon transitions are performed by the group of Bordé in Paris [11, 12, 13, 14] 200 kHz resolution in measurements on two photon transitions is achieved by Herlemont et al [15, 16] In both measurements saturation spectroscopy is performed in an absorption cell at room temperature

The onset of the quasicontinuum/stochastisation was investigated by Letokhov et al [4] and Alimpiev et al [17] Letokhov and coworkers utilized spontaneous Raman probing of the molecules excited by a pulsed $CO_2$ laser In the quasicontinuum the density of vibrational states is assumed to become sufficiently high so that within the experimental resolution levels overlap and interact so that the laser frequency does not have to fit a specific level to produce absorption In [4] the quasicontinuum is predicted to begin for energies exceeding 5000 $cm^{-1}$, for $SF_6$

Problems exist concerning the life time properties and energy distribution of the intermediate states excited during the MPE-process Energy transfer among those states by

collisions turns out to form an obstacle for dissociation In 1981 Bloembergen et al [18] utilized two independent 0 5 ns pulsed $CO_2$ lasers in a classic pump-probe experiment and observed a fast collisional scrambling rate for excited $SF_6$ molecules ($P\tau$=2 nsTorr) Thus studies of the states excited by the MPE process require highly rarefied conditions such as those present in a molecular beam environment

Molecular beam measurements were performed in the same years by A Giardini and coworkers [19] They observed spectral features resulting from MPE, MPD also was often found to possess spectral structure Continuously tunable infrared radiation produced with a high pressure pulsed $CO_2$ laser was used by Alimpiev et al [20] to measure the completely resolved frequency dependence of the MPE probability for bulk $SF_6$ at T=140 K and P=0 3 Torr A surprisingly structured spectrum was recorded and found to be very different from the smooth spectral envelopes resulting from measurements produced utilizing line tunable $CO_2$ lasers The spectrum of [20] contains several sharp peaks (0 15 $cm^{-1}$ FWHM), which have been assigned as Q-branches belonging to two and three photon resonances of the infrared active $\nu_3$ vibrational mode [9, 10]

Employing a sensitive bolometer as a detector [21] Boschetti et al [22] investigated the MPE probability of $SF_6$ as a function of the laser frequency of a line tunable TEA $CO_2$ laser At constant fluence of 1 $J/cm^2$, excitation spectra were measured for several stagnation conditions and shown to depend slightly on the rotational and strongly on the vibrational temperature of the $SF_6$ molecules At their most elevated stagnation temperature ($T_0$= 398 K) and at a laser frequency of 944 2 $cm^{-1}$ (10P20) the maximum absorption of an average of n=15 photons per molecule was observed At lower stagnation temperatures this maximum turned out to be lower (for $T_0$=198 K, n=7) and to occur at slightly less red shifted laser transitions (shifts up to 1 $cm^{-1}$) The envelope of these line tuned spectra shows resemblance with those collected by Schulz et al [23], measuring at a fluence of 5 $J/cm^2$ the MPD probability of $SF_6$ in a molecular beam Both series of spectra [22, 23] appear to be blue shifted in comparison with the spectra obtained in bulk experiments by Tsay et al [24]

C Liedenbaum et al [25, 26, 27] started to investigate MPE by c w lasers, in our laboratory Bolometric detection was employed to measure the energy deposited into the molecules by the laser interaction Up to five photons of about 1000 $cm^{-1}$ each, could be absorbed by the beam molecules before saturation occurred at about 1 $J/cm^2$ This saturation behaviour contrasted MPD observed with pulsed lasers and pointed to a different character of the laser-molecule interaction This difference was evidenced by the observation of multiphoton rapid adiabatic passage (RAP) prossesses due to the curved wave fronts of the tightly focussed c w $CO_2$ laser [27] Double resonance experiments demonstrated that RAP-MPE was an extremely narrow band phenomenon although the one-laser spectra appeared to be broad due to congestion [25]

The experiments in this thesis are restricted to the region below the quasicontinuum

One photon transitions are measured with very high accuracy by the group of Bordé [28] and recently by Herlemont et al [29] We cannot compete with their accuracies and accordingly no spectroscopy is performed on these transitions For the two photon transitions the group of Herlemont [15, 16] achieved a resolution of 200 kHz This is better than our resolution (2 MHz), however, we perform our measurements in a molecular beam in which low J-values are favoured [30, 31] Another difference between the measurements of [15, 16] and the measurements presented in this thesis are the spectral regions which are covered With the measurements utilizing two counterpropagating lasers interacting simultaneously with the $SF_6$ molecules (as presented in chapter 4 of this thesis) new spectral regions are covered in this way 95 new two photon transitions have been assigned

With the new method it is also possible to measure n-photon transitions with $n \geq 3$ with much higher accuracy than earlier measurements have achieved (for three photon transitions our resolution is 2 MHz, the measurements in [10] were performed with 30 MHz resolution) Due to selection rules it is possible to measure many more transitions utilizing multiphoton processes instead of overtone spectroscopy For overtone transitions leading to the third energy level, $\Delta J$=-1, 0 or 1 and the vibrational symmetry is restricted to $F_{1u}$, while for a three photon transition $\Delta J$ can be -3, -2, -1, 0, 1, 2 or 3 and the vibrational symmetry of the final level can be either $A_{2u}$, $F_{1u}$ or $F_{2u}$ With the same configuration with which the three photon transitions are measured it is also possible to measure transitions going to energie levels exceeding 3000 $cm^{-1}$ without loosing resolution

In this thesis the emphasis will be on the multiphoton spectroscopy of $SF_6$, in chapter 2 the measured frequencies obtained by measurements utilizing a $CO_2$ waveguide laser in combination with an Acousto Optic Modulator are presented The fitting procedure and results of this fit are presented in chapter 3 The experimental set-up utilized to investigate two colour, two photon transitions is described in section 4, the resulting transitions are presented and discussed in chapter 5 In chapter 6 an outlook is given on the experiments which can be done utilizing the new information presented in this thesis

Not only spectroscopy on $SF_6$ has been performed, some interesting general features are investigated and discussed through the thesis In chapter 2, RAP effects [27] are investigated in double resonance experiments Nearly 100% population inversion is observed for one and two photon transitions For the first time a two photon Rabi frequency is measured Io investigate which energy levels participate in the multiphoton process double resonance experiments are performed utilizing either an intra-cavity laser or a 150 Watt Apollo laser as a pump and a waveguide laser as a probe laser It seems that mainly transitions starting from already thermally excited $SF_6$ molecules contribute to the multiphoton signal while molecules in the ground state barely participate

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## Chapter 2

# One and two photon spectra of $SF_6$, molecular beam measurements

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## Abstract

Experiments on the saturation behaviour of one and two photon transitions have been performed on a molecular beam of $SF_6$-molecules, using single mode cw $CO_2$-lasers. Application of an Acousto Optic Modulator allowed a total tuning range of 0.6 GHz around each $CO_2$ laser line. Numerous, partially new absorptions have been observed and are catalogued. From the assigned transitions on the 10P16 laser line a rotational Boltzmann plot was derived showing strong deviation from a thermal distribution. Transitions from the RAP regime, with inversion, to the Rabi regime, with power broadening, have been observed, utilizing opto-thermal detection. A clear two photon Rabi frequency has been observed.

## 2.1 Introduction

The $\nu_3$-excitation of $SF_6$ has been widely studied by IR-spectroscopy it possesses a large transition strength and near coincidences with strong $CO_2$ laser lines [1-7] Theoretical effort has led to a good understanding of its spectral features including two and three photon transitions [8, 9, 10] Recently, multi-photon excitation spectra have been published showing featureless broadband absorption together with Rapid Adiabatic Passage (RAP) phenomena [11, 12, 13] Up to five $\nu_3$-photons were deposited into $SF_6$ by crossing a molecular beam with a cw $CO_2$ laser Opto thermal detection [14, 15] was applied to provide sensitive detection of the photons absorbed by the molecules The present study forms a continuation of the work of Liedenbaum et al [13]

Due to a number of refinements and extensions of the experimental set up (section 2), numerous one and two photon transitions became measurable with respect to recently published measurements [13, 16] The $CO_2$ wave guide laser was tuned over a range of 0 6 GHz around the $CO_2$ laser transitions utilizing an Acousto Optic Modulator as frequency shifter, with single and double passage of the laser beam Secondly, the laser intensity was amplified (by about a factor two) in a conventional 14 mm diameter discharge tube Third, the laser has been locked to a transmission peak of a Fabry Perot interferometer and has been scanned by changing the length of the Fabry-Perot cavity, the laser frequency was hereby stabilised to better than 1 MHz Fourth, the bolometer detector was cooled down to 1 7 K yielding a five fold improved signal to noise ratio as compared to its 4 2 K performance Spectra were taken around the 10P12 to 10P24 laser transitions

The P(4)-quadruplet one photon transition of $SF_6$ was predicted but observed before, for technical reasons, as a triplet only [1, 2] We succeeded in observing its fourth component at the expected spectral position confirming the predicted intensity ratio with respect to the other lines of the quadruplet Other very strong absorption signals were found due to two photon transitions, most of them could be assigned (see table $1^a$-$1^g$, section 3)

From all the assigned one and two photon transitions it is possible to derive a Boltzmann plot It indicates that the rotational cooling of molecules with high J-values ($J \geq 40$) is very poor ($T_{ROT} \approx 300$ K), this in contrast with the lowest observed J-values ($3 \leq J \leq 9$) for which a temperature of 5 K is obtained (section 3)

In section 4 we show that the transition from the RAP to the conventional Rabi regime can be made just by increasing the laser power, at maximum laser power the saturation regime is entered This is demonstrated with the help of the strong P(4) one photon transition which can easily be saturated, utilizing the double resonance technique When the fluence is low enough not to saturate the P(4) transition the FWHM is approximately 2 MHz Increasing the fluence by a factor 500 leads to considerable, but still limited line broadening A second effect is the decrease of the intensity by almost a factor 2, indicating that the transition from the RAP regime (with 100% population inversion) to the saturation

regime (in which eventually only 50% of the molecules are excited) occur

For two photon processes with a well defined initial and final state in a single mode/ single frequency field we found a quadratic power dependence This contrasts earlier studies of multi-photon transitions in $SF_6$ ( e g [11]), where no sharp spectral features were observed and the linear power dependence observed for non saturating fields has been explained by the high density of excited states, many pathways are available up to the fifth level, e g the bottleneck level [17]

The P(4) two photon transition, observed at +174 MHz from the line centre of the 10P16 $CO_2$ laser line, was used to investigate two photon Rabi oscillations The effect of having both RAP and Rabi processes in the same measurement, in variable proportions, is discussed For the first time a clear two photon Rabi oscillation was measured (section 5)

In section 6, the double resonance technique is applied to demonstrate the different degrees of saturation, for one and two photon processes

## 2.2 Experimental set-up

The molecular beam apparatus has been described before [11, 16] New are a Fabry-Perot Interferometer (FPI), an Acousto Optic Modulator (AOM), a $CO_2$ amplifier and the cooling of the bolometer temperature below 4 2 K The experimental set up is schematically drawn in figure 1

By modulating the length of the FPI with a piezo, using a split-off beam with about 10% of the laser power, the waveguide $CO_2$ laser could be locked to a well determined frequency The temperature controlled FPI consists of two spherical mirrors, f = 25 cm, reflectivity 99%, separated by 50 cm With its help the bandwidth of the wave guide laser could be reduced to 1 MHz, single mode operation was obtained and maintained since the reported results (sharp spectral features and background absorption) depend on this single mode operation The mode-structure of a waveguide laser is discussed in [18] The 230 MHz free spectral range (FSR) of the waveguide laser could be covered by scanning the etalon Along with the $CO_2$ radiation also a stabilised HeNe-laser [19] was aligned through the FPI in order to produce fringes (separated by 9 MHz) when the FPI was scanned In this way the relative frequency differences between absorption peaks could be determined with an accuracy of 1 MHz

An AOM (Intra Action Corp ) permits a frequency shift of 100 MHz This shift is achieved by reflections of the laser beam from moving Bragg planes , which are produced by an acoustic wave of 100 MHz in a germanium crystal The AOM can be used with single or double passage of the laser beam, the frequency is up or down shifted yielding shifts of +200, +100, -100 or -200 MHz Together with the FSR of the wave guide laser a tuning range of about 0 6 GHz around each $CO_2$ transition could thus be achieved Conversion efficiencies of nearly 55% of the incoming laser intensity have been realised, for every single

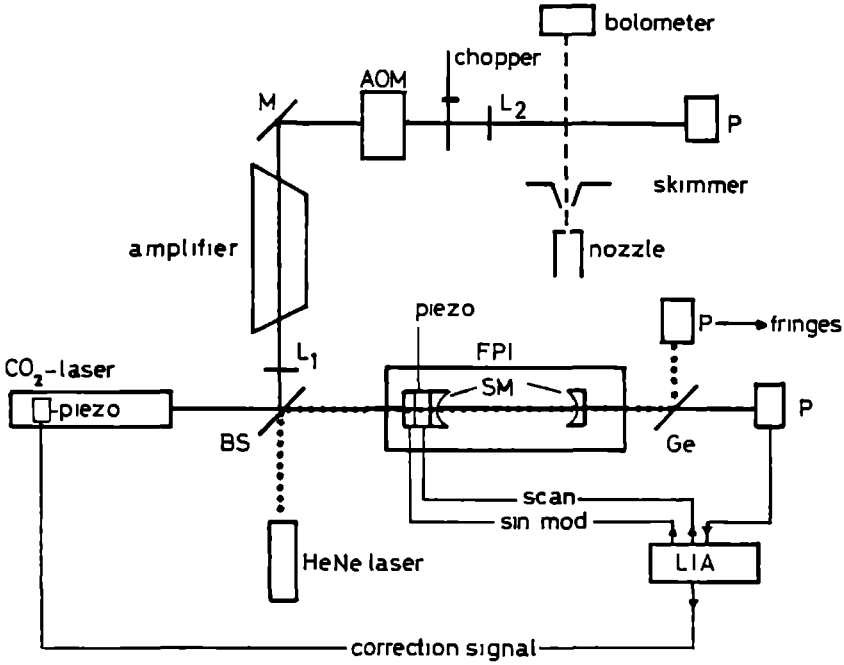


*Figure 1 Experimental set-up Bs = beamsplitter (R=90%), $L_{1,2}$ = lens ($f_1$ = 75 cm, $f_2$ = 20 cm), M = flat mirror, AOM = Acousto Optic Modulator, P = power meter, FPI = Fabry-Perot interferometer, SM = spherical mirror, Ge = Germanium plate, LIA = Lock-In amplifier*

pass

In order to increase the power of the waveguide laser (typical output power of 8 Watts) an amplifier was installed This amplifier consists of a 1 m long, water cooled $CO_2$ discharge tube with an inner diameter of 14 mm, flowed with a mixture of $CO_2$, He and $N_2$ Since the pressure of the gas mixture in the amplifier was about a factor 3 less as compared to the wave guide laser, the amplification was not constant for the total scanning range, at the center (edge) of the gain profile a maximum amplification factor 2 (1 2) has been achieved The resulting radiation has been focussed near to the crossing point with the molecular beam, to an approximate waist of 0 1 mm radius For the double pass configuration through the AOM, a maximum laser power of 5 Watts was obtained resulting in a fluence (i e laser intensity times interaction time) of 2 1 mJ/cm$^2$ for an average velocity of 1500 m/s of the seeded $SF_6$ molecules

The laser beam has been chopped for lock-in detection of the opto-thermal signal from a bolometer, sensitive to the energy of the molecules impinging on its cold surface By

cooling the bolometer from 4 2 K to approximately 1 7 K, the signal to noise ratio (S/N) is improved by a factor 5

Throughout the reported measurements the molecular beam conditions are characterised by a stagnation pressure $P_0$=1000 Torr and a stagnation temperature $T_0$=300 K, the nozzle diameter has been 50 $\mu$m and 2% $SF_6$ in He has been used

## 2.3 Experimental results

In fig 2 experimental results are presented for a frequency scan around the 10P16 $CO_2$-line Similar measurements are performed around the 10P12-10P24 $CO_2$-lines, the resulting data are listed in table $1^a$-$1^g$ Theoretically predicted lines from the literature (for the covered frequency region) are given The R(66) and the R(67) multiplets (10P12), the R(28)-quartet (10P14), the P(4)-quadruplet (10P16) and the P(33)-sextet (10P18), as measured by the Bordé-group [1, 2], served for absolute frequency calibration These are all one photon transitions For the 10P20 the relative distances between successive absorption lines were compared with the theoretically predicted distances to obtain an assignment and an absolute frequency calibration For the 10P22 and 10P24 the top of the laser gain profile (with amplifier) was used to estimate the line center frequency, resulting in an uncertainty of $\pm$ 5 MHz

Most of the earlier measured one photon [1, 2] and two photon transitions [9] in the $CO_2$ laser region 10P12-10P20 could be identified These authors could cover a frequency region of 500 MHz around a $CO_2$ line They achieved remarkably narrow linewidths by saturation spectroscopy Using bulk-gas absorption at room temperature they were able to excite molecules especially with high J-values, two photon resonances with large detunings (up to 50 GHz) were observed, however with the limitation $J \geq 14$ On the contrary we mainly observe two photon transitions on cold molecules ( $J \geq 3$) which are scarcely populated in bulk and have not been observed by Patterson *et al* [9] Transitions which were already measured by [1-7] and [9] are indicated by [1)] and [2)] respectively in table $1^a$-$1^g$, note that theoretical, not experimental results are listed

All one photon transitions have recently been recalculated by Bobin *et al* for $0 \leq J \leq 100$ [20] Agreement with earlier measurements [1, 2] exists within 1 MHz In our tables all calculated values for one photon transitions are taken from [20] Our measurements reproduce the earlier experimental results within 2 MHz At the limit of our tuning range about 20 new transitions were observed indicated by • in table $1^a$-$1^g$, these transitions agree with the calculation of [20] within 1 MHz One result of the extension of the tuning range with the aid of the AOM is the appearance of the fourth most blue shifted component of the P(4)-quadruplet (see section 4)

About 35 new two photon transitions were observed, especially for $J < 14$ Older experimental results on two photon transitions were obtained only for $J \geq 14$ transitions, these

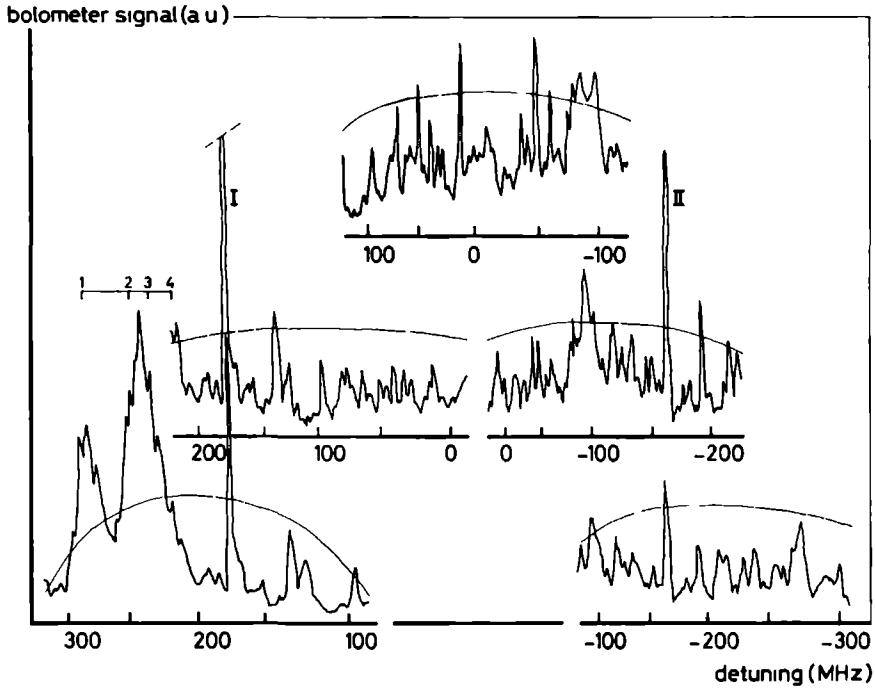


*Figure 2. Observed $SF_6$-spectra around the 10P16 $CO_2$ laser transition (947 7420 $cm^{-1}$) The frequency offset is given in MHz relative to the center of the laser line Notice the overlap and the non-linearity of the frequency scales The light lines on top give the laser power which at maximum is 2 5, 8 and 18 W for ±200 , ±100 and zero AOM-shift On the +200 MHz scan the positions of the P(4) one photon transitions are indicated The P(4) two photon transitions are indicated with I (+167 MHz) and II (-164 MHz) Note that the absolute signal strength can not be compared, between the different plots*

measured frequencies agree within 1 MHz with the calculated values Most of these transitions were also observed by us, with an uncertainty of 2 MHz Our new results can only be compared with a more extended, but older listing of Patterson [21] The deviation between the theoretical values and our new "low J-value" results, indicated by •• in table $1^a$-$1^g$, sometimes amounts up to 10 MHz Note that the published theoretical results [9] and the theoretical listing [21] are not identical, numerical differences amount to 1 MHz

and, for some high J-values, the assigned J-value differs by 2. Since the laser lines coincide mostly with one and two photon transitions of relatively high J-values (J≥35) not all of the calculated transitions could be observed; the main reason is that molecular levels with J-values ≥ 35 are hardly populated. Note that different authors use different conventions in characterising two photon transitions. Patterson gives the final J-value (and the final n-value) whereas Bobin et al. refer to the initial J-value. We have chosen for the latter

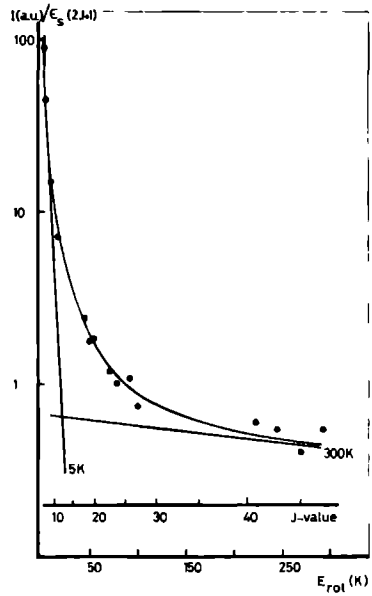


*Figure 3: The Boltzmann plot, derived from the equation* $I \sim \epsilon_S \cdot (2J+1) \cdot \exp\{-BJ(J+1)/kT\}$, *where I is the absorption strength,* $\epsilon_S$ *the symmetry weight (for* $F_1$, $F_2$, $E$, $A_1$, $A_2$ *respectively 6,6,8,2,10 [24]), J the rotational quantum number and B the rotational constant (0.09184* $cm^{-1}$ *[21]). The J-values of the first four points from left to right are* $J = 4$ , $J = 7$, $J = 9$ *and* $J = 11$ . *The four points with* $J \geq 40$ *correspond to one photon transitions, all other to two photon transitions. The error in the points with* $J \geq 40$ *( 25%) is much bigger than the error in the other points (5%). This is caused by two effects: first the intensity of a one photon transition is a factor two less compared to a two photon transition. Secondly, the poor population because of the high J-values decreases the signal, resulting in a smaller S/N ratio.*

convention and e g increased J by one unit for two photon P-transitions with respect to Patterson Rotational cooling is illustrated in a Boltzmann plot (fig 3) which was obtained from the relative intensities of the assigned one and two photon transitions around the 10P16 $CO_2$ laser line The one photon transitions with high J-values could only be observed with a "fresh" bolometer, i e before a layer of condensed $SF_6$ molecules started to decrease the sensitivity of the bolometer

The feature in fig 3 standing out is the non-Maxwellian rotational distribution of our expansion If one looks at the derivative of the Boltzmann-plot, for the lowest observed J-values a temperature of 5 K is obtained, in agreement with [22] However, for large J-values, J$\geq$40, the rotational cooling is very poor ($T_{ROT} \approx$300 K) Note that here the energy gap for two neighbouring J-states amounts to about 10 $cm^{-1}$ and more and causes inefficient cooling, this works in our favour, since otherwise we would not be able to observe transitions from levels with J$\geq$14 (for high J-values the level population decreases less than 10% by the expansion cooling) Evidently we have obtained a consistent set of level populations, derived from saturated one and two photon transitions

Based upon these results we can distinguish non saturated transitions, e g two photon transitions with a large detuning of the intermediate level In general, two photon resonances with detunings not exceeding 15 GHz (section 5) could be saturated for maximum laser powers using the $CO_2$ amplifier and the sharp focussing resulting in local laser intensities of 50 kW/cm$^2$ ($\Phi$ = 6 4 mJ/cm$^2$) In the case of larger detunings or less laser power (by using the AOM), only two photon transitions can be observed where the initial level is resonably populated, most of the two photon transitions with J<14 belong to this group Examples are the P(7)-doublet and the Q(9)-doublet (both 10P16 $CO_2$ line) which appear at the calculated spectral position within 10 MHz (fig 2)

Decreasing the laser power to 5 mW we were able to narrow the one photon transitions with low J-values, e g the P(4)-quadruplet An instrumental resolution of 2 MHz FWHM has been obtained Besides the 1 MHz bandwidth of the stabilized laser, another contribution comes from the Doppler residue of about 0 5 MHz for the collimated molecular beam The maximum obtainable fluence of waveguide laser plus amplifier hardly suffices to broaden the two photon transitions, thus resulting in small line widths On the other hand, all one photon transitions were significantly broadened, for maximum laser intensities To discriminate between one and two photon transitions the power dependence was measured as well as the line widths Note that the FWHM for one photon transitions at maximum fluence ( I = 50 kW/cm$^2$) still remains far below the value calculated from conventional power broadening expressions (FWHM $\approx \sqrt{2}\ \Omega^{(1)}_{\text{Rabi max}}/2\pi \approx$ 1 GHz [23])

From table 1 it follows that besides the assigned one and two photon resonances in the 10P12-10P20 region other spectral features show up Further, the presence of sharp resonances on the 10P22 and 10P24 lines were unexpected since these frequencies barely match with one or two photon steps on the $\nu_3$-ladder We believe that all unidentified

transitions belong to hot-band or combination-band transitions. We do not attribute these to three photon transitions. First, the intensity does not show the correct power dependence, secondly the laser power seems to be insufficient to overcome an acceptable "three photon detuning", as can be estimated from $\Delta_{1,2} \cdot \Delta_{2,3} = 2.5\ [\mathrm{GHz}]^2$ (see appendix), for maximum laser power of 15 Watts; here $\Delta_{1,2}(\Delta_{2,3})$ is the detuning of the first (second) intermediate level.

The occurrence of a combined RAP/Rabi-effect in the interaction of the laser beam with the molecules deserves special attention. Different alignments cause different portions of molecules to be excited by RAP- or Rabi-mechanisms, resulting in different lineshapes. Characteristic for a pure RAP effect is the doubled absorption intensity due to inversion (which is independent of the laser power within large limits as discussed in section 4) and the absence of power broadening. RAP transitions take place due to a frequency sweep as experienced by the molecules caused e.g. by the curved wave front in a Gaussian power profile normally encountered in a convergent or divergent laser beam; transitions of the Rabi-type occur in a constant frequency field, e.g. precisely in the focus of the laser beam [13, 15]. In order to get reproducible results standardized alignment procedures were followed.

For the Rabi-type transitions the laser focus was aligned to coincide with the molecular beam axis optimizing the cluster dissociation signal on the 10P8 $CO_2$ line ($P_0$=4.0

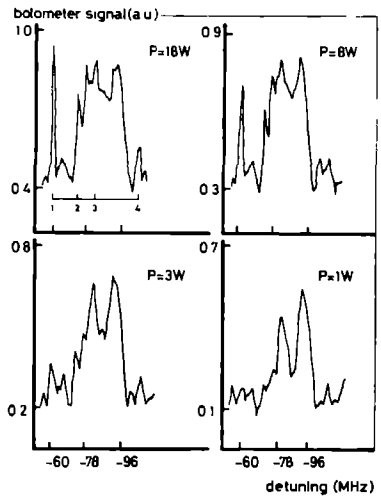


*Figure 4:"Blob" structure on the 10P16 $CO_2$ laser line. The numbers 1 to 4 mark the frequencies of respectively the Q(18), Q(25), Q(26) and Q(29) transitions (see table 1[c]).*

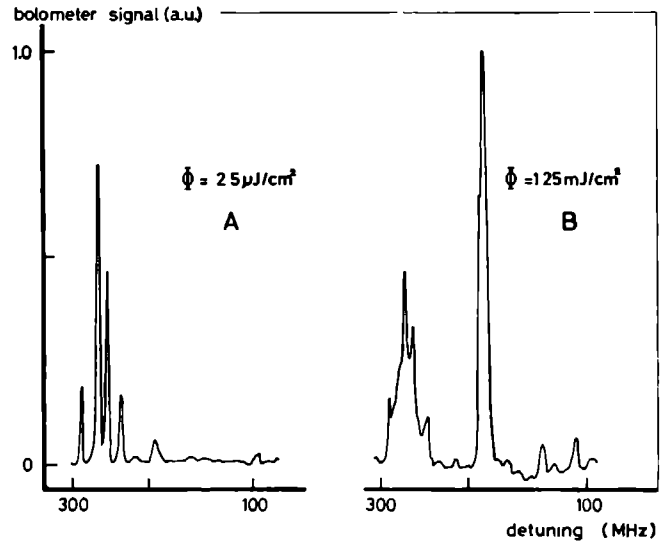


*Figure 5: From RAP regime, left, to Rabi regime, right, due to increasing power. The frequency offset is given in MHz relative to the 10P16 $CO_2$ laser-line. Note the non-linearity of the frequency-scale.*

bar, $T_0$=300 K, lens $L_2$ (fig.1) in "position B"). The alignment yielding maximum cluster dissociation ensures that the laser minimum waist is at the center of the molecular beam. Since the constant frequency condition in the laser focus is realized only for a limited dimension, it was not possible to suppress RAP-effects totally; because of the dimensions of the bolometer, 5 mm horizontal x 1 mm vertical, molecules cross the laser beam at different locations and partially "see" curved wave fronts.

Transitions of nearly pure RAP-type were realized by shifting the lens $L_2$ by 20 $\pm$ 5 mm to position A with respect to the optimum Rabi position discussed in the last paragraph; now all molecules interact with the curved wavefronts. The alignment was tested with well defined one and two photon transitions, showing an increase in intensity of more than 50 % when the lens $L_2$ was shifted from position B to A. One has to take into account the laser intensity which decreases when the lens is shifted, due to the divergence of the laser beam.

A remarkable fact is the appearance of "blobs" which show spectral sensitivity. These blobs appear, for growing laser power, on top of a relatively broad structure and are characterised by steep flanks as can be seen in fig.4. The blobs show up also at certain frequencies where at low laser power no absorption was observed.

## 2.4 The P(4) one-photon transitions

According to theoretical predictions, the quadruplet of P(4)- transitions, see fig.5[a], should show saturated intensities in the ratio of 1 : 3 : 4 : 3 [24]. Three of these transitions were observed before, with the best resolution of 10 kHz [1, 2]. The positions are shifted respectively 221 ($A_1(0)$), 238 ($F_1(0)$), and 250 (E(0)) MHz relative to the 10P16 $CO_2$ line (28,412,589 MHz) [25]. The observed relative line positions, see fig.5[a], lift any doubt that we deal with the P(4)-quadruplet. From the positions of the three well-known transitions, e.g. $A_1(0)$, $F_1(0)$, and E(0), we calibrate our frequency scale and observe a value of 286 ± 1 MHz for the fourth component ($F_2(0)$) of the P(4)-quadruplet. This position is in good agreement with the predicted value of [25]. To get an accurate estimate of the frequencies of the measured absorption lines, care has been taken to measure under RAP conditions, in order to avoid line broadening.

As for the intensities, note that the peak of the quadruplet shifted most to the blue in fig.5[a] is on the limit of the tuning range. With an improved alignment of the laser we were able to determine the relative intensities. Averaging a series of measurements yielded the ratio values 1 : 2.9 : 3.7 : 2.6 which are in good agreement with the theoretical ratios mentioned above. The intensities were measured under RAP-conditions, $L_2$ in position A, with a laser fluence of 0.4 $\mu J/cm^2$ (P = 5mW, $w = 0.5$ mm), enough to invert the population.

This value should be compared with the Rabi-frequency for a single $2\pi$ pulse, i.e. $\Omega^{(1)}_{Rabi} = \mu \cdot E_0/\hbar = 2\pi/\tau$ [$s^{-1}$] for Rabi-type transitions, lens $L_2$ in position B ($w_0 = 0.1$ mm). Here $\mu$ is the dipole moment, $\mu = 0.21$ Debye (for J = 4) [7], and $\tau$ is the transition time of the molecules through the laser field. The E-field in this equation can be expressed by $\sqrt{2P/\epsilon_0 c \pi w_0^2}$, where P is the laser power, $\epsilon_0$ the dielectric constant, $w_0$ the minimum laser beam radius and c the speed of light in vacuum. Substituting the appropriate values, we find a $2\pi$-cycle for a (circular) Rabi frequency for a one photon transition, $\Omega^{(1)}_{Rabi} = 50$ MHz for P = 3.2 mW. Note that the laser power for a $2\pi$-cycle is independent of $w \geq w_0$. The conclusion then is that slightly more power (ca. 30 %) than necessary for a $2\pi$-cycle yields almost complete inversion, under RAP conditions.

With a two laser pump and probe arrangement ($I_{pump} : I_{probe} = 7{:}3$ )we actually tested that inversion by the pump laser has been achieved for low laser power, leading to negative double resonance bolometer signals (fig.6) [11]. To make sure that we dealt here with transitions of the RAP-type and not with a $\pi$ pulse the laser fluence was doubled several times up to 13 $\mu J/cm^2$. No decrease of the signal was found, indicating the absence of Rabi oscillations. Double resonance experiments are discussed in detail in section 6.

When the laser intensity (I) and thus also the fluence ($\Phi$) is increased by a factor 500, two things happen to the one photon signals. First, considerable broadening is observed (but still less than expected for conventional power broadening), and second, the signals are reduced by about a factor two, as can be clearly seen in fig.5[b]. Both phenomena follow from

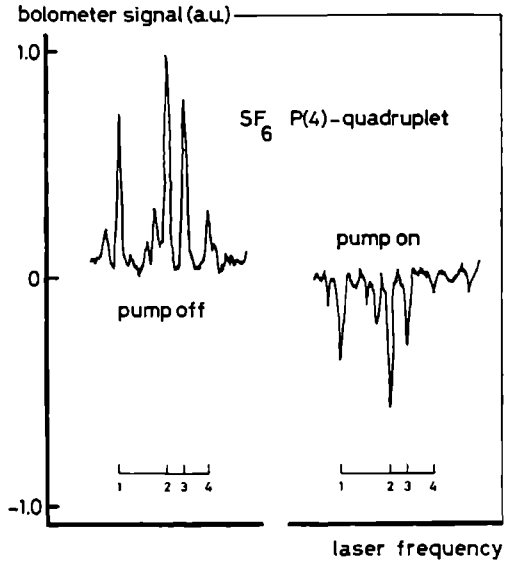


*Figure 6: Stimulated deexcitation of the $SF_6$ P(4)-quadruplet. On the left side the bolometer signal is shown for a (chopped) probe laser crossing the molecular beam. On the right an unchopped pump laser first produces inversion, resulting in stimulated deexcitation by the chopped probe laser. The positions of the P(4) lines are indicated with numbers 1 to 4.*

the fact that a change from the RAP regime to the (dephased) Rabi regime occurs by this drastic increase of laser intensity. In case of fig.5$^b$ the FWHM due to power broadening is found to be about 15 MHz. At the same time the inversion which is typical for RAP processes ceases to occur, thus a maximum of 50% population for the upper level is found; this explains the loss of signal strength in fig.5$^b$ as compared to fig.5$^a$. For a more detailed discussion of the RAP/Rabi transition see [26].

## 2.5 Two photon transitions with J$\leq$ 14

For a two photon transition the Rabi frequency can be estimated from the one photon Rabi frequency, $\Omega_R^{(2)} = \Omega_R^{(1)} \cdot \Omega_R^{(1)}/4\pi\Delta$ (see appendix). Using the saturation fluence of the P(4)-quadruplet (2.0 $\mu$J/cm$^2$) and maximum (amplified) laser power (section 2), it follows that two photon resonances with maximum detuning of respectively 15, 8 and 4 GHz can be saturated for the zero, single and double pass configuration of the AOM. This condition is illustrated for some two photon resonances on the 10P16 $CO_2$ line. Since many of the

two photon resonances with low J-value are found around this line we will restrict us here mainly to this spectral area (10P16 ± 0.3 GHz), if not mentioned otherwise.

The Q(9) doublet ($\Delta$ = 6 GHz) could only be saturated when focussing exactly on the molecular beam ($L_2$ in position B). The $F_1(0)$ component was observed at a position of +235 MHz, about 8 MHz red shifted relative to the calculated value of +227 MHz. The E(0) component at +170 MHz was found in better agreement with the theoretically predicted value of +167 MHz. Similar small discrepancies have been observed for the P(4) E(0) transition (which showed already some power broadening, because of the smaller detuning, $\Delta$ = 1.7 GHz) predicted at 164 MHz but observed at 174 MHz. Because of the saturation fluence of the P(4) transition, which is a factor 3 smaller than that of the Q(9) doublet, and the correct observed relative intensities of the Q(9) doublet, respectively 3:4, we are sure of this assignment. The P(4) $F_2(0)$ transition was also observed; it shows a redshift of 10 MHz relative to the predicted value. The P(7) $F_1(0)$ transition ($\Delta$ = 6.6 GHz) on top of the

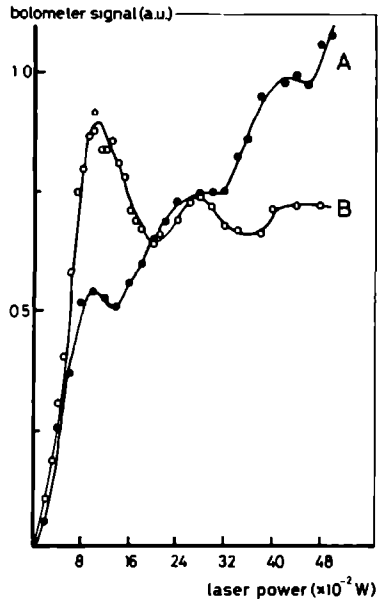


*Figure 7: Power dependence of the P(4) E(0) transition shifted 174 MHz from the 10P16 $CO_2$ line taken under two different conditions (i.e. alignments). Curve A: the laser is aligned to maximum bolometer signal of the P(4) transition (RAP conditions). Curve B: the laser is aligned to maximum cluster signal on top of the 10P8 $CO_2$ line (Rabi conditions).*

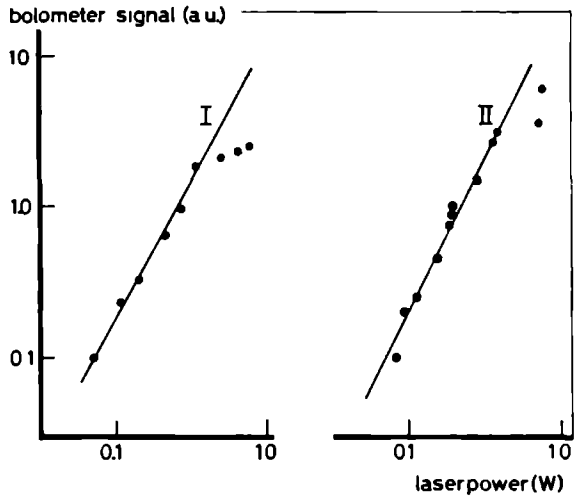


*Figure 8 Absorption signal for increasing laser power, for transition I and II of fig 2 For an isolated n-photon transition, the absorption signal is proportional to the $n^{th}$ power of the laser intensity The scales are logarithmic, the drawn lines correspond to n=2 Note that the laser fluence is smaller by about a factor 10 with respect to that of fig 7 due to different alignments*

P(4) quadruplet and the P(7) $F_2(0)$ ($\Delta$ = 2 2 GHz) were only observed with maximum laser intensity, at the expected spectral position (see table 1[c]) The S-type transitions ($\Delta J$ = +2) with relatively large detunings of 30 GHz (see table 1[c]) could only be observed with sub-saturation intensities

Because of the low saturation fluence of the P(4) E(0) transition the double resonance experiment could be repeated, for this two photon transition About 50% negative bolometer signal was found indicating 75% inversion Using this experimental set-up ($L_2$ in position A) the power dependence of the absorption intensity was investigated The result is shown in fig 7[a] Only a small remainder of a Rabi oscillation is observed When focussing again exactly on the molecular beam ($L_2$ position B) a much more pronounced Rabi oscillation was observed, indicating that we had entered the Rabi regime, fig 7[b] As far as we know this is the first time a two photon Rabi oscillation is observed Note the 50% increase of the "RAP saturation" going from $L_2$ position B to A

Dephasing behaviour of the oscillations results in a decreased absolute population (fig 7[b]), this is in good agreement with numerical calculations done in our laboratory using the

optical Bloch equations This simulation was performed using a Gaussian shaped intensity profile in a uniform frequency field An active participation of the intermediate level in the procces of populating the upper level is responsible for this behaviour, from this level both excitation to the two photon state and deexcitation to the ground state are possible Dephasing becomes very important when the intermediate detuning gets smaller than the power broadening of a one photon transition In case of random dephasing 33% of each level will be populated

From the Rabi frequency in fig 7[b] the power for the P(4) $2\pi$-pulse-transition could be calculated The measured value, 200 mW, differs about a factor two from the calculated value (see appendix, especially the last paragraph) Entering the sub-saturation domain, the quadratic response of a two photon transition is illustrated in fig 8

These two photon saturation measurements resemble the findings in [7] where similar experiments with one photon transitions were performed

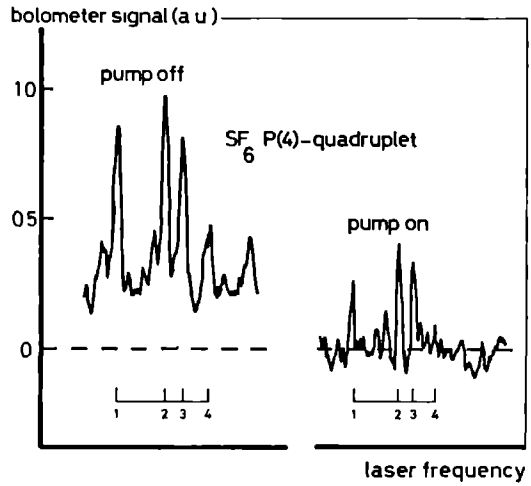


*Figure 9 Double resonance signal of the $SF_6$ P(4)-quadruplet ($P = 400\ mW$) On the left side the bolometer signal is shown for a (chopped) probe laser crossing the molecular beam On the right an unchopped pump laser first induces a Rabi oscillation corresponding roughly to the action of a $(2\pi n + \pi/3)$-pulse, yielding further excitation by the chopped probe laser, resulting in positive bolometer signal The positions of the P(4) lines are indicated with numbers 1 to 4*

## 2.6 Inversion vs saturation, illustrated by double resonance experiments

This section serves to demonstrate clearly, though qualitatively, RAP-processes and their (partial) disappearance for increasing laser power. To start we go back to fig.6, where for weak laser power of 10 mW (I = 1.3 W/cm$^2$, $\Phi$ = 8.5 $\mu$J/cm$^2$, $L_2$ in position A) RAP-inversion and stimulated deexcitation (by a second probe laser) are shown for the P(4)-quadruplet. Note the narrow line width and the 75% inversion obtained. In [11] similar one photon results were reported for a $C_2H_4$ -$\nu_7$- transition.

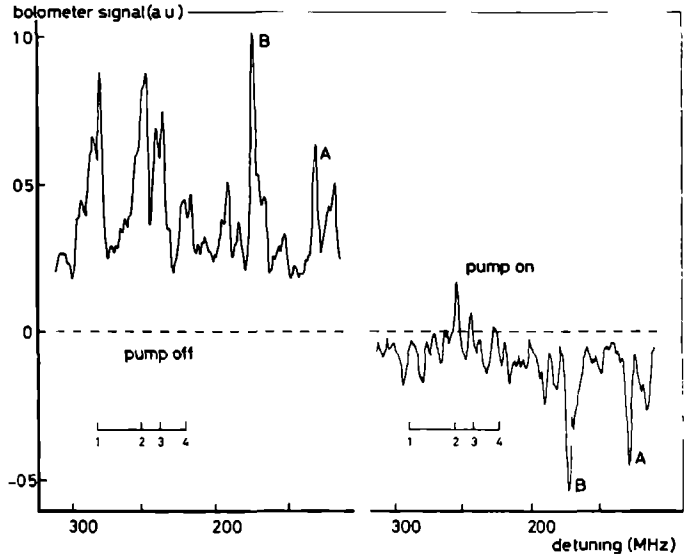


*Figure 10: Inversion vs. saturation on the 10P16 $CO_2$ laser line (+200 MIIz), for a laser power of 1.6 W. On the right side the two photon transitions A and B invert, while the P(4) one photon quadruplet is completely saturated, showing zero bolometer signal. The positions of the P(4) lines are indicated with numbers 1 to 4. The P(4) two photon transition is indicated with "B" whereas "A" is an unassigned two photon transition at 133 MHz detuned relative to the 10P16 $CO_2$ line center.*

Next, the experiment has been repeated with a laser power of 400 mW (I = 51 W/cm$^2$, $\Phi$ = 34 $\mu$J/cm$^2$, $L_2$ in position A), see fig.9. Two effects occur; most strikingly, the inversion (as proved by the negative signal in fig.6, with pump laser "on") is gone, for the P(4) quadruplet;

the RAP inversion starts disappearing at about 40 mW laser power. Secondly, some line broadening starts to show up. We take both effects as evidence for Rabi oscillations. The relative strength of the two laser signal of fig.9 suggests that the first laser excites about a 25% fraction of the ground state population with J = 4, i.e. the molecules see a $(2\pi n + \pi/3)$-pulse. The laser power of 400 mW corresponds to a n-value of about 11. Note that underneath the pump-off signal of fig.9 one observes a background, which has disappeared in the pump-on mode. Apparently the background stems from (the flanks of) many saturated one photon transitions.

Finally, the laser power was further increased to 1.6 W ($I = 200$ W/cm$^2$, $\Phi = 136$ $\mu$J/cm$^2$, $L_2$ in position A); the result is shown in fig.10. For the pump-off signal the P(4) quadruplet is still visible, but significantly broadened (although not to 1 GHz as expected conventionally [23]). The narrow peaks on top of the quadruplet probably are due to two photon transitions. The power is not large enough to saturate these transitions. Consequently, the left part of the pump-on signal averages to zero (the small peaks and valleys are not due to noise, but their origin is difficult to ascertain). Note that the laser power of 1.6 W corresponds to about 22 full Rabi cycles. On the left side of fig.10 interesting features start to appear. Peak B corresponds to the well assigned P(4)-two photon transition, 174 MHz detuned from the center of the 10P16 $CO_2$ laser transition, with the relative small $\Delta$-value of 1.7 GHz. This two photon transition is strongly inverted (i.e. not saturated in the conventional way);it shows about 75% inversion, yielding the negative signal for the pump-on mode. Analogously, peak A is determined as a two photon transition, which could not be assigned and probably therefore belongs to a hot band transition. Note the narrow line width of the two photon transitions and the background which disappears for the pump-on signal.

## 2.7 Outlook

There is one straightforward extension of the measurements discussed above. Since we were neither particularly successful with, nor especially interested in efficient expansion cooling, we did not change the $SF_6$ concentration in He. Increasing the concentration one can obtain stronger signals and longer interaction times (by diminishing the drift velocity). It looks interesting to investigate under these conditions the changes in the Boltzmann plot because $SF_6$-$SF_6$ collisions just after the nozzle become more important. We also will search further for isolated three photon transitions by increasing the laser fluence and by performing double resonance experiments.

Next, we will try to solve the riddle of the spectral blobs. The most interesting explanation to be found would be that for strong laser fluences we reach highly excited states which couple so strongly that local quasi-continua show up.

There has been another puzzling question we were not able to solve yet. Since we can virtually label states with every J-value up to 50, we tried to investigate which were the

ground state levels from which the molecules depart most easily during multi-photon excitation processes These experiments were more difficult than expected, we could not detect any ground state level with a very strongly preferent excitation probability Consequently we have to improve our detection sensitivity, there will be another attempt

Finally, experiments are underway to investigate the influence of high vibrational excitation on reactive and surface scattering properties in collaboration with the group of Duren in Gottingen and Iannotta in Trento, respectively, especially the angle distribution will be looked at

## 2.8 Table

Tabel 1[a] 10P12 $CO_2$ laser line 28,516,026 MHz

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 1 | | | | | -326 | 4 | w |
| 2 | | | | | -316 | 9 | w |
| 3 | | | | | -302 | 9 | w |
| 4 | | | | | -288 | 5 | w |
| 5 | R(93) $F_1(0)$,$F_2(0)$ | 1 | - | 285 | | | |
| 6 | | | | | -281 | 5 | w |
| 7 • | R(69) $F_1(2)$ | 1 | - | -270 | -271 | 2 | w |
| 8 • | R(68) $F_1(3)$ | 1 | - | -264 | 266 | - | w |
| 9 • | R(68) E(2) | 1 | - | -260 | -261 | 14 | w |
| 10 • | R(68) $F_2(3)$ | 1 | - | -256 | -257 | - | w |
| 11 | | | | | -249 | 5 | w |
| 12 | | | | | -244 | 3 | m |
| 13 | | | | | -239 | 3 | w |
| 14 | | | | | -235 | 3 | w |
| 15 | R(70) $F_2(7)$ | 1 | - | -231 | | | |
| 16 | | | | | -227 | 4 | w |
| 17 | | | | | -221 | 4 | w |
| 18 | | | | | -212 | 4 | m |
| 19 | | | | | -208 | 2 | w |
| 20 | | | | | -204 | 3 | w |
| 21 | | | | | -199 | 2 | w |
| 22 • | R(70) $F_1(7)$ | 1 | - | -190 | -190 | 5 | w |
| 23 | R(72) E(6),$F_2(10)$,$A_2(3)$ | 1 | - | -183 | | | |
| 24 | | | | | -175 | 6 | m |
| 25 [1)] | R(74) E(8),$F_2(12)$,$A_2(3)$ | 1 | - | -169 | -168 | 3 | m |
| 26 | | | | | -165 | 3 | w |
| 27 | | | | | -155 | 3 | w |
| 28 | | | | | -147 | 8 | m |
| 29 | | | | | -134 | 4 | w |
| 30 | | | | | -128 | 4 | w |
| 31 [1)] | R(89) E(0),$F_1(1)$,$A_1(0)$ | 1 | - | -117 | | | |
| 32 [1)] | R(73) E(4),$F_1(7)$,$A_1(2)$ | 1 | - | -113 | -112 | 9 | w |
| 33 | | | | | -101 | 4 | w |
| 34 | | | | | -93 | 5 | m |
| 35 | | | | | -79 | 4 | w |
| 36 | | | | | -63 | 8 | w |
| 37 | | | | | -60 | 8 | w |
| 38 | | | | | -50 | 4 | w |
| 39 | | | | | -29 | 3 | w |
| 40 [1)] | R(66) $F_1(0)$,$F_2(0)$,$A_1(0)$, $A_2(0)$ | 1 | - | -23 | -23 | 4 | m |
| 41 | | | | | -13 | 4 | w |
| 42 | | | | | -4 | 6 | m |
| 43 | | | | | 7 | 6 | w |
| 44 | | | | | 17 | 6 | w |
| 45 | | | | | 22 | 2 | w |
| 46 [1)] | R(83) E(1),$F_1(2)$,$A_1(0)$ | 1 | - | 25 | | | |
| 47 | | | | | 31 | 3 | w |
| 48 | | | | | 41 | 7 | m |
| 49 | | | | | 50 | 3 | w |
| 50 [1)] | R(77) $F_1(5)$,$F_2(4)$ | 1 | - | 54 | 54 | 3 | w |
| 51 | | | | | 63 | 3 | w |
| 52 | R(94) E(15),$F_2(23)$,$A_2(7)$ | 1 | - | 65 | | | |
| 53 | | | | | 70 | 3 | w |
| 54 | | | | | 74 | 3 | w |
| 55 | | | | | 79 | 3 | w |
| 56 | | | | | 87 | 7 | w |
| 57 | | | | | 90 | 4 | m |
| 58 | | | | | 99 | 4 | m |
| 59 | | | | | 103 | 2 | w |

tabel 1[a] (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 60 [1] | R(70) $A_1$(2) | 1 | - | 106 | 107 | 6 | w |
| 61 [1] | R(86) E(13),$F_1$(19),$A_1$(6) | 1 | - | 109 | | | |
| 62 | | | | | 121 | 3 | w |
| 63 | | | | | 127 | 10 | m |
| 64 | | | | | 139 | 6 | w |
| 65 | | | | | 143 | 2 | w |
| 66 | | | | | 148 | 2 | m |
| 67 | | | | | 150 | 2 | m |
| 68 | | | | | 156 | 4 | w |
| 69 | | | | | 162 | 2 | w |
| 70 | | | | | 166 | 2 | w |
| 71 | | | | | 171 | 5 | w |
| 72 | | | | | 178 | 3 | w |
| 73 • | R(69) $F_2$(12) | 1 | - | 187 | 185 | 10 | w |
| 74 [1] | R(70) $F_1$(6) | 1 | - | 197 | | | |
| 75 | | | | | 202 | 3 | w |
| 76 | R(71) $F_1$(9) | 1 | - | 209 | | | |
| 77 | R(69) E(8) | 1 | - | 210 | | | |
| 78 • | R(67) $F_1$(15),$F_2$(15),$A_1$(4), $A_2$(5) | 1 | - | 214 | 214 | - | m |
| 79 • | R(71) $F_2$(9) | 1 | | 220 | 219 | - | m |
| 80 | | | | | 221 | - | m |
| 81 • | R(69) $F_1$(13) | 1 | - | 228 | 227 | - | w |
| 82 | | | | | 230 | - | w |
| 83 | | | | | 234 | - | w |
| 84 • | R(81) $F_1$(3),$F_2$(3) | 1 | - | 240 | 241 | 5 | w |
| 85 | | | | | 244 | 5 | w |
| 86 | R(70) E(4) | 1 | - | 249 | | | |
| 87 | R(79) E(2),$F_2$(4),$A_2$(1) | 1 | - | 250 | | | |
| 88 | | | | | 254 | 3 | w |
| 89 | | | | | 261 | 5 | w |
| 90 | | | | | 266 | 4 | m |
| 91 | | | | | 272 | 3 | m |
| 92 | | | | | 288 | 4 | m |
| 93 | | | | | 294 | 2 | w |
| 94 | | | | | 297 | 2 | w |
| 95 | R(90) $F_1$(21) | 1 | | 308 | | | |

Tabel 1[b]: 10P14 $CO_2$ laser line 28,464,674 MHz

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 1 | | | | | -285 | 4 | m |
| 2 | | | | | -276 | 5 | m |
| 3 | | | | | -270 | 2 | w |
| 4 • | R(29) E(0),$F_1$(1),$A_1$(0) | 1 | | -264 | -264 | 12 | m |
| 5 | S(25) $F_1$(1) | 2 | 5.3 | -258 | | | |
| 6 | R(28) $F_1$(2) | 1 | - | -256 | | | |
| 7 | | | | | 252 | 9 | w |
| 8 | | | | | -245 | 3 | m |
| 9 | | | | | -241 | 4 | m |
| 10 •• | Q(40) E(4) | 2 | 14 | -231 | -233 | 2 | w |
| 11 | | | | | -225 | 3 | m |
| 12 •• | Q(30) $F_2$(2) | 2 | <1 | -220 | -220 | 9 | m |
| 13 •• | Q(30) $F_1$(1) | 2 | <1 | -216 | | | |
| 14 | Q(34) $F_2$(3) | 2 | 5 | -216 | | | |
| 15 | | | | | -211 | 5 | m |
| 16 | | | | | -203 | 2 | w |
| 17 | | | | | -193 | 9 | m |
| 18 | | | | | -182 | 2 | w |
| 19 | Q(34) $F_1$(3) | 2 | 5 | -178 | | | |
| 20 [1] | R(28) E(1) | 1 | - | -167 | -168 | 5 | m |
| 21 •• | R(18) E(2) | 2 | 15 | 160 | -160 | 9 | m |

Tabel 1[8]. (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 22 | S(52) $A_1(2)$ | 2 | 31 | -158 | | | |
| 23 | | | | | -152 | 2 | m |
| 24 [1] | R(28) $F_2(2)$ | 1 | - | -144 | -143 | 4 | m |
| 25 | | | | | -138 | 2 | m |
| 26 | S(52) E(4) | 2 | 31 | -134 | | | |
| 27 | S(53) $A_2(1)$ | 2 | 31 | -130 | | | |
| 28 | S(53) E(3) | 2 | 31 | -128 | | | |
| 29 •• | R(6) E(0) | 2 | 33 | -125 | -126 | - | m |
| 30 | | | | | -115 | 6 | m |
| 31 [2] | S(47) $F_2(9)$ | 2 | 29 | -94 | -94 | 3 | w |
| 32 | | | | | -89 | 3 | w |
| 33 [2] | S(46) $F_1(1)$ | 2 | 28 | -79 | -79 | 6 | w |
| 34 [2] | S(46) E(0) | 2 | 28 | -77 | | | |
| 35 [2] | S(46) $F_2(1)$ | 2 | 28 | -74 | | | |
| 36 | Q(37) $A_1(1)$ | 2 | 10 | -73 | | | |
| 37 [2] | S(47) E(6) | 2 | 29 | -72 | | | |
| 38 | | | | | -71 | 3 | m |
| 39 | R(58) E(7),$A_2(3)$ | 2 | 34 | -64 | | | |
| 40 | | | | | -62 | 2 | w |
| 41 | | | | | -58 | 2 | w |
| 42 | | | | | -54 | 2 | w |
| 43 [2] | S(47) $F_1(10)$ | 2 | 29 | -53 | | | |
| 44 | | | | | -49 | 2 | w |
| 45 •• | R(6) $F_1(1)$ | 2 | 34 | -43 | -42 | 3 | w |
| 46 •• | Q(39) $A_1(1)$ | 2 | 11 | -35 | -36 | 2 | w |
| 47 | | | | | -31 | 4 | w |
| 48 | | | | | -20 | 2 | w |
| 49 | | | | | -16 | 2 | w |
| 50 | | | | | -13 | 2 | w |
| 51 | | | | | -9 | 2 | w |
| 52 | | | | | 0 | 4 | w |
| 53 | | | | | 5 | 2 | w |
| 54 | | | | | 13 | 2 | w |
| 55 [1] | R(28) $A_2(0)$ | 1 | - | 18 | 18 | 5 | m |
| 56 | | | | | 29 | 5 | m |
| 57 | | | | | 34 | 2 | w |
| 58 [1] | R(28) $F_2(1)$ | 1 | - | 39 | 39 | 5 | m |
| 59 [1] | R(28) $F_1(1)$ | 1 | - | 55 | 55 | 5 | m |
| 60 | Q(46) $F_1(10)$ | 2 | 25 | 66 | | | |
| 61 [1] | R(28) $A_1(0)$ | 1 | - | 68 | 68 | 10 | w |
| 62 | Q(46) E(6) | 2 | 25 | 71 | | | |
| 63 | Q(46) $F_2(10)$ | 2 | 25 | 75 | | | |
| 64 | Q(56) $A_1(3)$ [-] | 2 | 40 | 78 | | | |
| 65 | | | | | 80 | 10 | w |
| 66 | | | | | 93 | 3 | w |
| 67 | | | | | 101 | 10 | w |
| 68 | | | | | 112 | 2 | w |
| 69 | | | | | 117 | 2 | w |
| 70 [2] | S(48) $F_1(3)$ | 2 | 29 | 119 | | | |
| 71 | | | | | 122 | 5 | m |
| 72 | | | | | 128 | 5 | m |
| 73 | | | | | 132 | 5 | m |
| 74 | | | | | 138 | 5 | m |
| 75 | | | | | 148 | 2 | w |
| 76 | | | | | 158 | 2 | w |
| 77 | | | | | 162 | 2 | m |
| 78 | | | | | 167 | 4 | s |
| 79 | | | | | 176 | 2 | w |
| 80 [1] | R(29) $F_1(2)$,$F_2(1)$ | 1 | - | 185 | 185 | 5 | m |
| 81 | | | | | 193 | 2 | w |
| 82 | | | | | 198 | 2 | w |

Tabel 1[5]: (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 83 •• | R(6) $A_1$(0) | 2 | 34 | 217 | 217 | 2 | w |
| 84 | | | | | 225 | 2 | w |
| 85 | S(50) E(2) | 2 | 29 | 228 | | | |
| 86 | | | | | 228 | 2 | w |
| 87 •• | Q(14) E(1) | 2 | 20 | 234 | 237 | 10 | m |
| 88 | S(47) E(7),$F_1$(11),$F_2$(11) | 2 | 25 | 237 | | | |
| 89 | S(51) $F_1$(7) | 2 | 30 | 244 | | | |
| 90 | | | | | 239 | 2 | m |
| 91 | | | | | 247 | 2 | w |
| 92 | | | | | 253 | 4 | m |
| 93 | | | | | 264 | 4 | w |
| 94 | | | | | 271 | 4 | m |
| 95 | | | | | 276 | 2 | w |
| 96 •• | R(18) $F_1$(4) | 2 | 16 | 282 | 281 | 2 | w |
| 97 | S(50) $F_2$(3) | 2 | 29 | 291 | | | |
| 98 | | | | | 291 | 2 | w |
| 99 | Q(14) $F_2$(2) | 2 | 20 | 296 | | | |
| 100 | | | | | 302 | 2 | w |

Tabel 1[c]: 10P16 $CO_2$ laser line 28.412,590 MHz

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 1 | Q(44) $F_2$(2) | 1 | - | -320 | | | |
| 2 •• | Q(23) $F_2$(5) | 2 | 4.8 | -297 | -300 | - | m |
| 3 • | Q(46) E(2) | 1 | - | -291 | -291 | - | w |
| 4 | Q(30) $A_2$(0) | 2 | 4 2 | -288 | | | |
| 5 | Q(44) $A_2$(0) | 1 | - | -288 | | | |
| 6 | R(42) E(3) | 2 | 1 3 | -278 | | | |
| 7 •• | Q(31) E(4) | 2 | 2 4 | 276 | -277 | - | s |
| 8 •• | P(7) $F_2$(0) | 2 | 4 7 | -269 | -267 | - | m |
| 9 | S(11) $F_2$(1) | 2 | 27 | -269 | | | |
| 10 •• | Q(27) $A_1$(1) | 2 | 3 7 | -255 | -256 | | m |
| 11 [1] | Q(55) $F_2$(6) | 1 | - | -249 | | | |
| 12 | R(37) $F_1$(6),$F_2$(7) | 2 | <1 | -246 | | | |
| 13 [1] | Q(55) $F_1$(6) | 1 | - | -242 | | | |
| 14 •• | Q(31) $F_1$(7) | 2 | 2 4 | -238 | -237 | | |
| 15 •• | Q(30) $F_2$(0) | 2 | 3 7 | -237 | -237 | - | s |
| 16 | R(42) $F_1$(5) | 2 | 1.3 | -229 | | | |
| 17 •• | Q(29) $F_2$(6) | 2 | 4 2 | -227 | | | |
| 18 •• | Q(25) $F_2$(5) | 2 | 4.5 | -226 | -228 | - | s |
| 19 [1] | Q(46) $F_1$(3) | 1 | - | -213 | | | |
| 20 •• | Q(26) $F_1$(0) | 2 | 4 0 | -210 | -210 | - | - |
| 21 [1] | Q(49) $F_1$(7) | 1 | - | -207 | | | |
| 22 •• | Q(28) $F_1$(0) | 2 | 4.2 | -206 | -205 | - | s |
| 23 | R(52) $F_2$(3) | 2 | <1 | -205 | | | |
| 24 [1] | Q(47) $F_1$(7) | 1 | - | -193 | -195 | - | - |
| 25 •• | Q(16) $F_1$(0) | 2 | 6 0 | -186 | -191 | - | s |
| 26 •• | Q(30) $F_1$(0) | 2 | 3.6 | -189 | -187 | - | - |
| 27 | | | | | -181 | - | m |
| 28 | | | | | -177 | - | |
| 29 [2] | Q(21) $F_1$(5) | 2 | 5.1 | -172 | -174 | 2 | m |
| 30 | | | | | -170 | 1 | - |
| 31 •• | P(4) $F_2$(0) | 2 | 0.35 | -173 | -164 | 2 | s |
| 32 [2] | Q(29) E(4) | 2 | 3 3 | -162 | | | |
| 33 [2] | R(46) $F_2$(7) | 2 | <1 | -160 | | | |
| 34 [1] | Q(49) E(4) | 1 | - | -159 | | | |
| 35 [2] | Q(24) $F_2$(0) | 2 | 4 5 | -155 | -156 | - | - |
| 36 [2] | R(47) E(2) | 2 | <1 | -152 | | | |
| 37 [2] | Q(27) $F_1$(6) | 2 | 3 6 | -149 | -151 | | m |
| 38 [1] | Q(54) $A_2$(2) | 1 | - | -147 | | | |
| 39 [2] | Q(14) $F_1$(0) | 2 | 6.3 | -144 | -146 | | - |
| 40 [2] | Q(30) $A_1$(0) | 2 | 3 6 | -141 | | | |

Tabel 1°: (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 41 •• | R(42) $A_1(2)$ | 2 | 1.4 | -140 | -141 | - | - |
| 42 1) | Q(54) $F_2(7)$ | 1 | - | -137 | -136 | - | m |
| 43 1) | Q(54) E(4) | 1 | - | -132 | | | |
| 44 2) | R(24) $F_1(0)$,$F_2(0)$ | 2 | 4.4 | -132 | | | |
| 45 2) | Q(28) E(0) | 2 | 4.0 | -128 | -127 | 2 | m |
| 46 | R(52) E(2) | 2 | <1 | -127 | | | |
| 47 1) | Q(41) $F_1(9)$ | 1 | - | -122 | -122 | 2 | - |
| 48 1) | Q(41) E(5) | 1 | - | -117 | -118 | 2 | s |
| 49 1) | Q(48) $F_1(4)$ | 1 | - | -115 | -115 | 2 | - |
| 50 1) | Q(41) $F_2(8)$ | 1 | - | -111 | -111 | 2 | m |
| 51 2) | Q(29) $F_1(7)$ | 2 | 3.2 | -103 | -103 | 2 | s |
| 52 | | | | | -96 | 6 | s |
| 53 | S(20) E(3),$F_1(4)$,$A_1(1)$ | 2 | 40 | -87 | | | |
| 54 | | | | | -86 | 4 | s |
| 55 2) | Q(44) $F_1(5)$ | 2 | <1 | -81 | -81 | 5 | - |
| 56 2) | Q(26) E(0) | 2 | 3.9 | -79 | -79 | 2 | s |
| 57 2) | Q(25) E(3) | 2 | 4.1 | -75 | -75 | 2 | m |
| 58 | S(19) $A_2(0)$ | 2 | 39 | -71 | | | |
| 59 | | | | | -70 | 2 | w |
| 60 | S(19) $F_2(1)$ | 2 | 39 | -66 | | | |
| 61 1) | Q(45) $A_2(2)$ | 1 | - | -63 | -65 | 4 | w |
| 62 2) | Q(18) $F_2(0)$ | 2 | 5.6 | -60 | -62 | - | s |
| 63 | | | | | -59 | 2 | s |
| 64 2) | Q(27) $F_2(6)$ | 2 | 3.5 | -52 | | | |
| 65 2) | Q(28) $F_2(0)$ | 2 | 4.0 | -51 | -51 | 5 | s |
| 66 2) | Q(22) E(0) | 2 | 4.8 | -50 | | | |
| 67 | R(52) $F_1(3)$ | 2 | <1 | -50 | | | |
| 68 | | | | | -46 | - | s |
| 69 2) | Q(23) E(3) | 2 | 4.5 | -39 | -38 | - | m |
| 70 2) | R(45) $A_2(1)$ | 2 | <1 | -34 | -35 | - | - |
| 71 1) | Q(53) $F_2(6)$ | 1 | - | -30 | -30 | - | - |
| 72 | | | | | -25 | - | - |
| 73 1) | Q(53) $F_1(6)$ | 1 | - | -17 | -18 | - | s |
| 74 1) | Q(38) $F_2(0)$ | 1 | - | -8 | | | |
| 75 1) | Q(38) E(0),$F_1(0)$ | 1 | - | -7 | -8 | 10 | w |
| 76 | | | | | -2 | - | m |
| 77 •• | R(49) $A_2(2)$ | 2 | <1 | 2 | 3 | - | w |
| 78 •• | Q(11) $F_1(1)$ | 2 | 6.5 | 8 | 10 | 2 | s |
| 79 1) | Q(43) $F_1(8)$ | 1 | - | 9 | | | |
| 80 1) | Q(45) $F_2(7)$ | 1 | - | 13 | | | |
| 81 •• | S(11) E(0) | 2 | 27 | 24 | 20 | 3 | w |
| 82 2) | Q(24) $F_1(0)$ | 2 | 4 3 | 27 | 25 | 2 | s |
| 83 2) | Q(26) $F_2(0)$ | 2 | 3 8 | 32 | 30 | 2 | s |
| 84 2) | R(35) $F_1(4)$ | 2 | <1 | 33 | | | |
| 85 1) | Q(48) $F_2(5)$ | 1 | - | 36 | | | |
| 86 2) | R(35) $F_2(5)$ | 2 | <1 | 36 | | | |
| 87 2) | Q(27) $A_2(2)$ | 2 | 3.4 | 38 | 37 | 2 | s |
| 88 1) | Q(43) E(5) | 1 | - | 38 | | | |
| 89 | | | | | 43 | 2 | m |
| 90 2) | Q(19) E(2) | 2 | 5.3 | 50 | 48 | 2 | s |
| 91 | | | | | 52 | - | - |
| 92 | | | | | 56 | 2 | m |
| 93 | | | | | 62 | 2 | m |
| 94 2) | Q(20) E(0) | 2 | 4.4 | 71 | 70 | 2 | s |
| 95 2) | Q(25) $F_1(6)$ | 2 | 4.0 | 72 | 72 | 2 | s |
| 96 1) | Q(43) $F_2(8)$ | 1 | - | 72 | | | |
| 97 1) | Q(47) E(4) | 1 | - | 73 | | | |
| 98 2) | R(43) $F_2(5)$ | 2 | <1 | 81 | 79 | 2 | m |
| 99 1) | Q(52) E(4) | 1 | - | 86 | 86 | 2 | w |
| 100 1) | Q(52) $F_1(6)$ | 1 | - | 95 | 93 | 8 | - |
| 101 | | | | | 96 | 3 | s |

Tabel 1[c] (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 102 [1] | Q(46) $A_1$(1) | 1 | - | 96 | | | |
| 103 [1] | Q(45) $F_1$(8) | 1 | - | 100 | 100 | 4 | - |
| 104 •• | S(12) $F_1$(3) | 2 | 28 | 103 | 102 | 8 | w |
| 105 [1] | Q(52) $A_1$(2) | 1 | - | 112 | 110 | 2 | w |
| 106 | | | | | 116 | 2 | - |
| 107 | | | | | 122 | 3 | s |
| 108 | | | | | 125 | 3 | m |
| 109 | | | | | 133 | 4 | s |
| 110 [2] | Q(21) $F_2$(4) | 2 | 4.8 | 142 | 142 | 2 | s |
| 111 [1] | Q(47) $F_1$(7) | 1 | - | 147 | 147 | 2 | - |
| 112 [2] | Q(23) $F_1$(5) | 2 | 4.4 | 153 | 152 | 2 | s |
| 113 | | | | | 160 | - | w |
| 114 | | | | | 168 | 6 | s |
| 115 •• | Q(9) E(0) | 2 | 6 8 | 167 | 170 | 2 | s |
| 116 •• | P(4) E(0) | 2 | 0 076 | 164 | 174 | 2 | s |
| 117 •• | Q(24) $A_1$(0) | 2 | 4 1 | 188 | 185 | 4 | m |
| 118 | | | | | 192 | 6 | s |
| 119 [1] | Q(51) $F_2$(6) | 1 | - | 206 | 207 | 6 | m |
| 120 •• | Q(22) $F_2$(0) | 2 | 4 5 | 214 | 215 | - | - |
| 121 [1] | P(4) $A_1$(0) | 1 | - | 221 | 221 | - | s |
| 122 •• | Q(9) $F_1$(1) | 2 | 6 4 | 227 | 235 | - | s |
| 123 [1] | Q(51) $F_1$(6) | 1 | - | 228 | | | |
| 124 [1] | P(4) $F_1$(0) | 1 | - | 238 | 238 | | s |
| 125 [1] | Q(40) $A_1$(0) | 1 | - | 247 | 245 | | - |
| 126 [1] | P(4) E(0) | 1 | - | 250 | 250 | | s |
| 127 [1] | Q(45) $A_1$(2) | 1 | - | 251 | | | |
| 128 •• | P(7) $F_1$(0) | 2 | 5 3 | 252 | 254 | | - |
| 129 [1] | Q(40) $F_1$(1) | 1 | - | 253 | | | |
| 130 | R(38) $F_1$(0) | 2 | <1 | 257 | | | |
| 131 • | Q(40) $F_2$(1) | 1 | - | 259 | 259 | | m |
| 132 | R(38) $F_2$(0) | 2 | <1 | 260 | | | |
| 133 • | Q(40) $A_2$(0) | 1 | - | 266 | 265 | | - |
| 134 | R(53) E(6) | 2 | <1 | 267 | | | |
| 135 | R(49) $F_2$(7) | 2 | <1 | 273 | | | |
| 136 | R(39) $F_2$(3) | 2 | <1 | 276 | | | |
| 137 • | Q(47) $A_2$(2) | 1 | - | 276 | 276 | | |
| 138 | Q(46) $F_1$(4) | 1 | - | 282 | | | |
| 139 | S(12) E(1) | 2 | 28 | 286 | | | |
| 140 • | P(4) $F_2$(0) | 1 | - | 286 | 286 | | s |
| 141 | R(39) $F_2$(3) | 2 | <1 | 289 | | | |
| 142 •• | R(47) $A_2$(2) | 2 | <1 | 293 | 295 | | w |
| 143 | Q(50) $A_2$(1) | 1 | - | 313 | | | |

Tabel 1[d] 10P18 $CO_2$ laser line 28,359,774 MHz

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 1 | | | | | -315 | 4 | m |
| 2 | | | | | -308 | 4 | m |
| 3 | | | | | -297 | 4 | m |
| 4 | R(21) $F_2$(2) | 2 | 69 | 290 | | | |
| 5 | | | | | -290 | 8 | w |
| 6 | | | | | 283 | 2 | w |
| 7 | P(42) $F_1$(6) | 2 | 19 | -278 | | | |
| 8 | P(57) E(0),$A_1$(0) | 2 | 52 | 277 | | | |
| 9 | | | | | -274 | 10 | m |
| 10 | P(49) E(1),$F_2$(2),$A_2$(0) | 2 | 31 | 288 | | | |
| 11 | | | | | -266 | 8 | m |
| 12 | P(42) $F_2$(6) | 2 | 19 | -262 | | | |
| 13 | P(37) $F_2$(5) | 2 | 7 7 | 260 | | | |
| 14 | | | | | 259 | 2 | w |
| 15 | | | | | -252 | 10 | w |
| 16 | | | | | -243 | 5 | m |

Tabel 1[d]: (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 17 | | | | | -231 | 5 | m |
| 18 | P(39) $F_2$(5) | 2 | 12 | -227 | | | |
| 19 | P(35) $F_1$(6) | 2 | 3 5 | -221 | | | |
| 20 | | | | | -217 | - | - |
| 21 | O(26) $F_2$(1) | 2 | 14 | -215 | -212 | - | - |
| 22 | | | | | -207 | - | - |
| 23 | | | | | -203 | - | - |
| 24 | | | | | -198 | - | - |
| 25 | | | | | -190 | 6 | m |
| 26 | | | | | -174 | 3 | s |
| 27 | O(11) $A_2$(0) | 2 | 41 | -169 | | | |
| 28 | | | | | -168 | 2 | m |
| 29 | | | | | -163 | 2 | s |
| 30 | | | | | -161 | 2 | s |
| 31 | | | | | -154 | 2 | w |
| 32 | R(21) $F_1$(2) | 2 | 59 | -150 | | | |
| 33 | | | | | -149 | 3 | w |
| 34 | | | | | -144 | 3 | w |
| 35 | | | | | -139 | 2 | w |
| 36 | Q(55) E(0),$A_2$(0) **) | 2 | 43 | -137 | | | |
| 37 | | | | | -134 | 6 | m |
| 38 [2] | O(26) E(2) | 2 | 13 | -130 | | | |
| 39 [2] | O(26) $F_2$(4) | 2 | 13 | -126 | | | |
| 40 [1] | P(33) $F_1$(5) | 1 | - | -126 | -127 | 2 | - |
| 41 | | | | | -123 | 2 | m |
| 42 [2] | O(26) $A_2$(1) | 2 | 13 | -117 | | | |
| 43 [1] | P(32) $F_1$(6),$F_2$(7) | 1 | - | -117 | -117 | 4 | m |
| 44 | | | | | -115 | 2 | w |
| 45 | | | | | -112 | 2 | w |
| 46 | | | | | -109 | 2 | w |
| 47 | | | | | -107 | 2 | w |
| 48 | | | | | -102 | - | m |
| 49 | | | | | -100 | - | m |
| 50 | | | | | -98 | - | m |
| 51 | | | | | -91 | 2 | m |
| 52 | | | | | -88 | 2 | m |
| 53 [1] | P(33) $F_2$(4) | 1 | - | -85 | -85 | 3 | m |
| 54 | | | | | -81 | 4 | m |
| 55 | | | | | -75 | 2 | w |
| 56 | | | | | -69 | 2 | w |
| 57 | R(22) $F_2$(3) | 2 | 59 | -62 | | | |
| 58 | | | | | -62 | 2 | w |
| 59 | | | | | -59 | 2 | m |
| 60 | | | | | -54 | 2 | w |
| 61 | | | | | -49 | 6 | m |
| 62 | | | | | -42 | 2 | w |
| 63 | | | | | -39 | 2 | w |
| 64 | | | | | -36 | 2 | w |
| 65 | | | | | -30 | 2 | w |
| 66 | | | | | -28 | 3 | m |
| 67 | | | | | -25 | 2 | w |
| 68 | | | | | -17 | 5 | m |
| 69 •• | P(39) $F_1$(4) | 2 | 12 | -15 | -13 | 2 | w |
| 70 | | | | | -7 | 4 | m |
| 71 | | | | | -2 | 2 | w |
| 72 | | | | | 3 | 2 | w |
| 73 [1] | P(33) $A_2$(1) | 1 | - | 6 | 7 | - | m |
| 74 | | | | | 14 | 2 | w |
| 75 | | | | | 18 | 4 | w |
| 76 | | | | | 31 | 10 | m |
| 77 | | | | | 45 | 2 | w |

Tabel 1[d] (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 78 | | | | | 49 | 5 | m |
| 79 | | | | | 53 | 2 | w |
| 80 | P(45) $F_1(3)$,$F_2(3)$ | 2 | 28 | 55 | | | |
| 81 | | | | | 63 | 10 | m |
| 82 | | | | | 68 | 2 | w |
| 83 | | | | | 75 | 4 | w |
| 84 | | | | | 80 | 4 | w |
| 85 | | | | | 85 | 2 | w |
| 86 | | | | | 89 | 2 | w |
| 87 | | | | | 91 | 4 | m |
| 88 | | | | | 95 | 2 | w |
| 89 | R(18) E(0) | 2 | 60 | 98 | | | |
| 90 | | | | | 99 | 3 | m |
| 91 | P(36) $A_1(1)$ | 2 | 6 0 | 102 | | | |
| 92 | R(18) $F_1(1)$ | 2 | 60 | 105 | | | |
| 93 [1)] | P(33) $F_2(5)$ | 1 | | 108 | 107 | 2 | w |
| 94 | | | | | 113 | 9 | m |
| 95 | P(19) $A_2(0)$ | 2 | 26 | 114 | | | |
| 96 | P(20) $A_1(0)$ | 2 | 27 | 119 | | | |
| 97 | | | | | 121 | 2 | w |
| 98 | | | | | 126 | 5 | w |
| 99 | | | | | 130 | 2 | w |
| 100 | R(24) $F_2(5)$ | 2 | 57 | 131 | | | |
| 101•• | P(35) $A_1(1)$ | 2 | 3 5 | 138 | 136 | 2 | w |
| 102 | | | | | 140 | 9 | m |
| 103[1)] | P(33) E(3) | 1 | - | 141 | | | |
| 104 | | | | | 147 | 2 | w |
| 105 | | | | | 150 | 2 | w |
| 106 | | | | | 156 | 3 | m |
| 107 | | | | | 160 | 2 | w |
| 108 | | | | | 162 | 2 | w |
| 109 | R(24) E(3) | 2 | 57 | 163 | | | |
| 110 | | | | | 166 | 2 | w |
| 111 | | | | | 170 | 2 | w |
| 111 | R(16) $F_1(0)$ | 2 | 59 | 171 | | | |
| 112 | R(16) $F_2(0)$ | 2 | 59 | 174 | | | |
| 113 | | | | | 175 | 2 | w |
| 114 | | | | | 180 | 3 | m |
| 115 | | | | | 184 | 3 | m |
| 116 [1)] | P(33) $F_1(6)$ | 1 | | 187 | 188 | 2 | w |
| 117 | R(24) $F_1(5)$ | 2 | 57 | 191 | | | |
| 118 •• | P(32) $F_2(1)$ | 2 | 2 1 | 193 | 193 | 4 | w |
| 119 | | | | | 197 | 2 | w |
| 120 | | | | | 203 | 2 | w |
| 121 | | | | | 208 | 3 | m |
| 122 | | | | | 215 | 2 | w |
| 123 | | | | | 219 | 3 | m |
| 124 | | | | | 224 | 3 | m |
| 125 •• | O(14) $F_1(2)$ | 2 | 35 | 231 | 230 | | w |
| 126 | | | | | 237 | - | - |
| 127 | | | | | 240 | 2 | m |
| 128 | | | | | 246 | 6 | m |
| 129 | | | | | 252 | 2 | w |
| 130 | | | | | 255 | | m |
| 131 | | | | | 260 | | w |
| 132 | R(22) E(2) | 2 | 59 | 260 | | | |
| 133 | | | | | 264 | - | - |
| 134 | | | | | 272 | 2 | w |
| 135 | | | | | 277 | 2 | w |
| 136 •• | P(32) E(1) | 2 | 2 1 | 275 | 278 | 2 | m |
| 137 | | | | | 284 | 2 | m |
| 138 | | | | | 290 | 2 | w |

Tabel 1[d]. (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 139 | | | | | 295 | - | w |
| 140 | | | | | 297 | 2 | w |
| 141 | | | | | 302 | 4 | w |
| 142 | | | | | 304 | 2 | m |
| 143 | | | | | 312 | 2 | w |

Tabel 1[e]. 10P20 $CO_2$ laser line 28,306,225 MHz

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 1 | | | | | -317 | 4 | w |
| 2 | | | | | -311 | 3 | w |
| 3 | | | | | -299 | 4 | w |
| 4 | Q(50) $F_1(7)$ -) | 2 | 12 | -298 | | | |
| 5 | | | | | -294 | 4 | w |
| 6 | Q(50) $F_2(6)$ -) | 2 | 12 | -294 | | | |
| 7 | O(8) E(0) | 2 | 103 | -292 | | | |
| 8 | Q(37) $F_1(4)$ --) | 2 | 42 | -279 | | | |
| 9 | Q(42) E(6),$F_1(8)$,$A_1(3)$ --) | 2 | 31 | -279 | | | |
| 10 | | | | | -274 | 4 | w |
| 11 | | | | | -268 | 2 | w |
| 12 | | | | | -258 | 3 | m |
| 13 | Q(49) E(1),$F_1(3)$ -) | 2 | 15 | -258 | | | |
| 14 | Q(49) $F_2(2)$ -) | 2 | 15 | -257 | | | |
| 15 | | | | | -244 | 4 | m |
| 16 | | | | | -231 | 2 | w |
| 17 1) | P(57) $F_1(3)$,$F_2(3)$ | 1 | - | -226 | | | |
| 18 | O(25) $F_2(1)$ | 2 | 72 | -223 | | | |
| 19 | | | | | -216 | 4 | m |
| 20 | Q(51) $F_1(7)$,$F_2(8)$ -) | 2 | 10 | -209 | | | |
| 21 | | | | | -207 | 4 | m |
| 22 | | | | | -203 | 3 | w |
| 23 1) | P(58) $F_1(8)$,$F_2(9)$ | 1 | - | -197 | | | |
| 24 | | | | | -191 | 3 | w |
| 25 | Q(50) E(4),$F_1(6)$,$A_1(2)$ -) | 2 | 12 | -185 | | | |
| 26 | | | | | -183 | 3 | w |
| 27 | O(20) $F_2(0)$ | 2 | 79 | -175 | | | |
| 28 | | | | | -165 | 3 | w |
| 29 | | | | | -159 | 3 | w |
| 30 | | | | | -150 | 2 | w |
| 31 2) | Q(43) E(0),$F_2(1)$,$A_2(0)$ --) | 2 | 29 | -148 | | | |
| 32 | O(47) E(1),$F_1(2)$,$A_1(0)$ | 2 | 22 | -146 | | | |
| 33 | Q(49) $F_1(5)$ | 2 | 19 | -144 | | | |
| 34 | O(47) $F_2(4)$ | 2 | 22 | -143 | | | |
| 35 1) | P(59) $F_1(9)$ | 1 | - | -141 | -141 | 3 | w |
| 36 2) | Q(49) $A_2(3)$ -) | 2 | 15 | -134 | | | |
| 37 2) | Q(49) $F_2(10)$-) | 2 | 15 | -131 | | | |
| 38 2) | Q(49) $F_1(11)$ -) | 2 | 15 | -126 | | | |
| 39 | | | | | -125 | 2 | w |
| 40 2) | Q(49) $A_1(3)$ -) | 2 | 15 | -121 | | | |
| 41 | Q(37) $F_2(5)$ --) | 2 | 42 | -115 | | | |
| 42 | | | | | -115 | 3 | w |
| 43 | | | | | -100 | 3 | m |
| 44 | P(14) E(0) | 2 | 89 | -92 | | | |
| 45 | Q(38) $F_2(3)$ --) | 2 | 40 | -78 | | | |
| 46 1) | P(60) $F_1(1)$ | 1 | - | -75 | | | |
| 47 1) | P(60) E(0),$F_2(1)$ | 1 | - | -74 | -74 | 5 | w |
| 48 1) | P(59) $F_2(9)$ | 1 | - | -72 | | | |
| 49 2) | Q(49) $F_1(7)$ -) | 2 | 15 | -66 | | | |
| 50 2) | Q(44) E(7),$F_1(10)$,$A_1(3)$ --) | 2 | 26 | -64 | | | |
| 51 | P(30) $F_1(2)$ | 2 | 59 | -64 | | | |
| 52 | P(30) $F_2(1)$ | 2 | 59 | -63 | | | |
| 53 2) | Q(49) E(4) -) | 2 | 15 | -58 | | | |

Tabel 1[a] (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 54 | | | | | 56 | 3 | m |
| 55 [2)] | Q(49) $F_1(10)$ | 2 | 15 | -54 | | | |
| 56 [2)] | Q(49) E(5) | 2 | 15 | 50 | | | |
| 57 | Q(38) $F_1(3)$ [**)] | 2 | 40 | -49 | | | |
| 58 | | | | | 46 | 5 | m |
| 59 [2)] | Q(49) E(6) | 2 | 15 | -45 | | | |
| 60 | O(46) E(6),$F_1(9)$,$A_1(3)$ | 2 | 27 | -41 | | | |
| 61 [2)] | Q(50) $F_1(5)$,$F_2(5)$ [*)] | 2 | 12 | -37 | | | |
| 62 | | | | | -35 | 4 | w |
| 63 | | | | | -19 | 5 | m |
| 64 [2)] | Q(52) E(5),$F_2(8)$,$A_2(2)$ [**)] | 2 | 7 5 | -19 | | | |
| 65 [2)] | Q(49) $F_2(9)$ [*)] | 2 | 15 | -17 | | | |
| 66 [2)] | Q(53) E(2),$F_1(4)$,$A_1(1)$ [**)] | 2 | 5 0 | -14 | | | |
| 67 | | | | | -10 | 3 | m |
| 68 | O(25) E(0) | 2 | 68 | 2 | | | |
| 69 [2)] | Q(49) $F_1(6)$ [*)] | 2 | 15 | 2 | 2 | 3 | m |
| 70 | | | | | 9 | 3 | m |
| 71 | | | | | 15 | 2 | w |
| 72 | | | | | 26 | 4 | m |
| 73 [1)] | P(59) $A_2(3)$ | 1 | | 28 | | | |
| 74 | | | | | 32 | 2 | w |
| 75 [2)] | Q(51) E(3),$F_1(5)$,$A_1(1)$ [**)] | 2 | 10 | 40 | | | |
| 76 | | | | | 48 | 2 | w |
| 77 | | | | | 55 | 3 | w |
| 78 [2)] | Q(54) E(6),$F_2(10)$,$A_2(3)$ [**)] | 2 | 2 5 | 60 | 63 | 3 | w |
| 79 [2)] | Q(49) $A_2(1)$ [*)] | 2 | 15 | 61 | | | |
| 80 | Q(49) E(3) [*)] | 2 | 15 | 64 | | | |
| 81 [2)] | Q(49) E(5) | 2 | 15 | 66 | | | |
| 82 [2)] | Q(49) $F_2(7)$ [*)] | 2 | 15 | 67 | | | |
| 83 [2)] | Q(49) $F_2(8)$ | 2 | 15 | 70 | | | |
| 84 [2)] | Q(49) E(6) [*)] | 2 | 15 | 72 | | | |
| 85 [2)] | Q(49) $A_2(2)$ [*)] | 2 | 15 | 75 | | | |
| 86 [2)] | Q(49) $F_2(9)$ [*)] | 2 | 15 | 76 | | | |
| 87 | | | | | 80 | 4 | w |
| 88 [1)] | P(55) $F_1(0)$,$F_2(0)$ | 1 | - | 88 | 88 | 2 | w |
| 89 [2)] | Q(49) $A_2(3)$ [*)] | 2 | 15 | 89 | | | |
| 90 | Q(19) $F_1(0)$ | 2 | 79 | 91 | | | |
| 91 | Q(19) $F_2(0)$ | 2 | 79 | 92 | | | |
| 92 | | | | | 100 | 4 | m |
| 93 | | | | | 112 | 4 | m |
| 94 [1)] | P(56) E(8),$F_2(12)$,$A_2(3)$ | 1 | - | 128 | | | |
| 95 | | | | | 129 | 3 | w |
| 96 [2)] | Q(48) $F_1(0)$,$A_1(0)$ [*)] | 2 | 17 | 131 | | | |
| 97 [2)] | Q(48) $F_2(0)$,$A_2(0)$ [*)] | 2 | 17 | 132 | | | |
| 98 | | | | | 134 | 4 | w |
| 99 | | | | | 141 | 4 | w |
| 100 [2)] | Q(39) $F_1(3)$ [**)] | 2 | 38 | 147 | | | |
| 101 | P(35) $F_2(3)$ | 2 | 49 | 148 | | | |
| 102 | O(31) E(4),$F_2(7)$,$A_2(2)$ | 2 | 57 | 149 | | | |
| 103 | | | | | 149 | 2 | w |
| 104 [2)] | Q(39) $F_2(3)$ [**)] | 2 | 38 | 151 | | | |
| 105 [2)] | Q(50) E(4),$F_2(6)$,$A_2(1)$ [*)] | 2 | 12 | 154 | | | |
| 106 | | | | | 155 | 4 | w |
| 107 | | | | | 161 | 4 | m |
| 108 [2)] | Q(49) $F_1(8)$,$F_2(7)$ [*)] | 2 | 15 | 175 | | | |
| 109 | | | | | 179 | 3 | m |
| 110 | | | | | 196 | 4 | m |
| 111 | | | | | 209 | 8 | m |
| 112 | Q(55) E(8),$A_1(3)$ [**)] | 2 | <1 | 212 | | | |
| 113 | Q(36) $F_1(4)$ [**)] | 2 | 44 | 217 | | | |
| 114 | | | | | 223 | 2 | w |

Tabel 1[e]: (continued)

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 115 | O(43) $F_1(0)$,$F_2(0)$ | 2 | 28 | 224 | | | |
| 116 [1)] | P(59) $F_2(10)$ | 1 | - | 226 | | | |
| 117 | O(27) $F_1(3)$ | 2 | 65 | 230 | | | |
| 118 | | | | | 240 | 2 | w |
| 119 | Q(48) $F_2(8)$ [-)] | 2 | 17 | 243 | | | |
| 120 | | | | | 243 | 3 | m |
| 121 | Q(48) E(5) [-)] | 2 | 17 | 247 | | | |
| 122 | | | | | 250 | 3 | w |
| 123 | Q(48) $F_1(8)$ [-)] | 2 | 17 | 253 | | | |
| 124 | | | | | 258 | 4 | w |
| 125 | O(50) $F_2(5)$ | 2 | 19 | 261 | | | |
| 126 | | | | | 265 | 3 | w |
| 127 | P(59) E(6) | 1 | - | 270 | | | |
| 128 | | | | | 283 | 2 | w |
| 129 | O(8) $F_2(0)$ | 2 | 100 | 287 | | | |
| 130 | | | | | 291 | 3 | w |
| 131 | O(20) $F_1(0)$ | 2 | 79 | 300 | | | |
| 132 | | | | | 300 | 2 | w |
| 133 | | | | | 308 | 3 | w |

Tabel 1[f]: 10P22 $CO_2$ laser line 28,251,942 MHz

| nr | transitions | n | Δ [GHz] | $\nu_{th}$ [MHz] | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|
| 1 | | | | | -276 | 4 | m |
| 2 | | | | | -263 | 3 | m |
| 3 | | | | | -252 | 3 | m |
| 4 | | | | | -240 | 3 | m |
| 5 | | | | | -231 | 4 | m |
| 6 | | | | | -222 | 4 | m |
| 7 | | | | | -205 | 4 | s |
| 8 | P(83) $F_1(13)$ | 1 | - | -192 | | | |
| 9 | | | | | -185 | 4 | s |
| 10 | | | | | -173 | 4 | s |
| 11 | | | | | -161 | 3 | m |
| 12 | | | | | -153 | 5 | m |
| 13 | | | | | -133 | 3 | m |
| 14 | | | | | -119 | 3 | m |
| 15 | | | | | -105 | 6 | m |
| 16 | P(82) $F_1(10)$ | 1 | - | -86 | | | |
| 17 | | | | | -75 | 3 | w |
| 18 | | | | | -45 | 3 | w |
| 19 | | | | | -23 | 4 | m |
| 20 | | | | | 39 | 4 | w |
| 21 | | | | | 49 | 3 | w |
| 22 | P(81) $F_1(8)$,$F_2(7)$ | 1 | - | 58 | | | |
| 23 | P(83) $F_2(14)$ | 1 | - | 114 | | | |
| 24 | P(83) $F_1(14)$ | 1 | - | 236 | | | |
| 25 | | | | | 237 | 5 | w |
| 26 | | | | | 285 | 3 | m |

Tabel 1[9]. 10P24 $CO_2$ laser line 28,196,923 MHz

| nr | $\nu_{exp}$ [MHz] | FWHM [MHz] | I | nr | $\nu_{exp}$ [MHz] | FWHM [MHz] | I | nr | $\nu_{exp}$ [MHz] | FWHM [MHz] | I |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | -297 | 3 | m | 14 | -8 | 3 | m | 27 | 180 | 3 | s |
| 2 | -286 | 3 | w | 15 | -1 | 3 | m | 28 | 184 | 3 | s |
| 3 | -279 | 3 | w | 16 | 17 | 4 | m | 29 | 188 | 3 | m |
| 4 | -271 | 3 | m | 17 | 37 | 3 | m | 30 | 208 | 4 | m |
| 5 | -248 | 9 | w | 18 | 53 | 5 | s | 31 | 223 | 4 | m |
| 6 | -221 | 3 | m | 19 | 71 | 5 | m | 32 | 232 | 2 | m |
| 7 | -203 | 5 | m | 20 | 80 | 7 | s | 33 | 241 | 3 | m |
| 8 | -164 | 4 | m | 21 | 95 | 5 | m | 34 | 257 | 3 | m |
| 9 | -150 | 3 | m | 22 | 123 | 3 | m | 35 | 265 | 2 | m |
| 10 | -135 | 4 | m | 23 | 140 | 3 | m | 36 | 264 | 4 | m |
| 11 | -113 | 4 | m | 24 | 147 | 4 | w | 37 | 272 | 3 | m |
| 12 | -41 | 3 | w | 25 | 159 | 2 | m | 38 | 278 | 3 | m |
| 13 | -23 | 3 | m | 26 | 167 | 3 | s | | | | |

*Table 1: All calculated $SF_6$ one [20] and two [9, 21] photon transitions around the 10P12 to 10P24 $CO_2$ laser lines (each ± 320 MHz) are listed in column two, with their symmetry type. If more than one symmetry is given, different transitions coincide within our accuracy; earlier measured one photon transitions, [1, 2], are indicated by [1)], the two photon transitions, [9], by [2)]. The newly measured one and two photon transitions which we could assign are marked with • and ••, respectively. The Q-transitions marked with [*)] indicate $\Delta l = 0$; the [**)] indicates that both $\Delta l = 0$ and $\Delta l = 2$ transitions coincide within our accuracy. If there is no indication, only a $\Delta l = 2$ transition is present. The number of photons participating in the transition is given in column three. The fourth and fifth column show respectively the calculated [9, 20] and measured frequencies in MHz relative to the center of the $CO_2$ laser line. The center frequencies are taken from [28]. The intensity in the seventh column gives only a rough indication of the strength of the absorption lines relative to each other; w = weak, m = medium, s = strong.*

## 2.9 Appendix

The n-photon Rabi frequencies, $\Omega_R^{(n)}$, are related approximately to the one photon Rabi frequency, $\Omega_R^{(1)}$, by [27]

$$\frac{\Omega_R^{(n)}}{2} = \frac{\Omega_R^{(1)}}{2} \cdot \left( \frac{\Omega_R^{(1)}}{2 \cdot 2\pi\Delta} \right)^{n-1} \tag{2.1}$$

In equation 1, the one photon frequencies are taken to be step- independent; similarly, the intermediate levels are assumed to posses the same (average) detuning $\Delta$.

We will use equation 1 to estimate the maximum acceptable $\Delta$-value, for two and three photon processes (in view of our maximum realized laser power $P_{max}$ = 15 Watts) and to

find the laser power for which typically a two photon $2\pi$-Rabi cycle is expected.

For maximum laser power ($P_{max}$) equation 1 becomes

$$\Omega_R^{(n)}(P_{max}) = \Omega_{R,s}^{(1)} \cdot \left(\frac{P_{max}}{P_{1,s}}\right)^{n/2} \cdot \left(\Omega_{R,s}^{(1)}\right)^{n-1} \cdot (4\pi\Delta)^{1-n} \tag{2.2}$$

$\Omega_{R,s}^{(1)}$ stands for the one photon Rabi frequency at the laser power $P_{1,s}$, where a $2\pi$-pulse is completed during the interaction time, $\tau = 130$ ns. Next we multiply both sides of equation 2 by $\tau$ and put $\Omega_{R,s}^{(1)} \cdot \tau = \Omega_R^{(n)}(P_{max}) \cdot \tau$, i.e. we postulate a $2\pi$-Rabi cycle for $P_{max}$. Then

$$(4\pi\Delta)^{n-1} = \left(\frac{P_{max}}{P_{1,s}}\right)^{n/2} \cdot \left(\Omega_{R,s}^{(1)}\right)^{n-1} \tag{2.3}$$

For n = 2, the acceptable detuning is given already in section 5. For n = 3 we derive $\Delta \leq 2.5$ GHz in order to find at least a $2\pi$-Rabi cycle.

The two photon Rabi frequency for which a $2\pi$-cycle is performed during $\tau$, corresponds to a laser power $P_{2,s}$. We then find from equation 1

$$4\pi\Delta = \frac{P_{2,s}}{P_{1,s}} \cdot \Omega_{R,s}^{(1)} \tag{2.4}$$

For the P(4) two photon transition, $\Delta$ amounts to 76 MHz. From here follows that $P_{2,s}$ is approximately 100 mW. If this result is compared to the position of the first minimum in fig.7[b], at 200 mW, we find a factor 2 discrepancy, which is acceptable for these measurements because the focused laser intensity is not well known.

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## Chapter 3

# Calculation of two photon transitions in $SF_6$, fit to measured frequencies

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## Abstract

Two photon transitions of the $\nu_3$ band of $SF_6$ have been fit utilizing two different representations of the Hamiltonian The strong transitions predicted around the 10P16 $CO_2$ laser line can all be observed within 3 MHz from the calculated frequencies For the other measured spectral regions (i e the regions around the 10P12, 10P14, 10P18, 10P20, 10P22 and 10P24 $CO_2$ laser lines), we are less certain of the assignment of the two photon transitions, because in these regions almost no strong lines are predicted The constants utilized to produce the best fit of the two photon transitions are presented

## 3.1 Introduction

In this paper an updated table of the $2\nu_3$ transitions of $SF_6$ will be discussed. A table of calculated and measured one and two photon transitions was already presented in [1]; however, in that case our measured frequencies where not included in the fitting procedure. In the meantime two fitting programs for the measured two photon transitions were developed; both methods start from the same Hamiltonian, which will be discussed in section 2, but utilize different representations of the tensorial components in this Hamiltonian.

In section 3 the difference in the results of the two fitting procedures will be discussed. In the fitting procedure also transitions measured with two different lasers interacting simultaneously with the molecules are included. These measurements are discussed elsewhere [2]. In order to make it possible to compare the theoretically predicted strengths of the transitions with the measured ones, we included a multiplication factor for each J-value. This multiplication factor is derived from the Boltzmann plot presented in fig.3 of [1]. From this we know that we deal with a non thermal rotational energy distribution; therefore it is possible to measure transitions with J-values up to approximately 40, if their strength factors are large enough. Of course, the transitions starting from low J-values are much easier to observe in our set-up utilizing a molecular beam. In section 4 the results of the fitting procedure will be discussed.

## 3.2 Calculation of two photon transitions

$$H = \sum H_{(i)}, with \tag{3.1}$$

| | | | | | | energy (J=10) |
|---|---|---|---|---|---|---|
| $H_{(0)}=$ | $H_{02}+$ | $H_{20}$ | | | | 1000 $cm^{-1}$ |
| $H_{(1)}=$ | | $H_{21}$ | | | | 1 $cm^{-1}$ |
| $H_{(2)}=$ | $H_{04}+$ | $H_{22}+$ | $H_{40}$ | | | 1 $cm^{-1}$ |
| $H_{(3)}=$ | | $H_{23}+$ | $H_{41}$ | | | $10^{-3}$ $cm^{-1}$ |
| $H_{(4)}=$ | $H^{\odot}_{06}+$ | $H^{\odot}_{24}+$ | $H_{42}+$ | $H_{60}$ | | $10^{-2}$ $cm^{-1}$ |
| $H_{(5)}=$ | | $H^{\odot}_{25}+$ | $H_{43}+$ | $H^{\star}_{61}$ | | $10^{-5}$ $cm^{-1}$ |
| $H_{(6)}=$ | $H^{\odot}_{08}+$ | $H_{26}+$ | $H_{44}+$ | $H^{\star}_{62}+$ | $H^{\star}_{80}$ | $10^{-6}$ $cm^{-1}$ |
| $H_{(7)}=$ | | $H^{\odot}_{27}+$ | $H^{\star}_{45}+$ | $H^{\star}_{63}+$ | $H^{\star}_{81}$ | $10^{-10}$ $cm^{-1}$ |
| | | | 1 | 2 | 3 | |

In [3, 4] a general way to write down the Hamiltonian for the rotations and vibrations of a molecule is proposed. Starting from these conventions it is possible to calculate the

energy levels and eigenfunctions describing the ro-vibrational behaviour of the $\nu_3$-mode in $SF_6$ [5].

Eq.1 represents the Hamiltonian split into the different orders ($H_{(0)}$ second order, $H_{(1)}$ third order, etc.). $H_{ij}$ means that the vibration parameters are of order i and the rotation parameters are of order j. For example $H_{20}$ represents the pure vibration, $v\hbar\omega$ with $\hbar\omega$ the energy of one vibrational quantum and $v$ the number of vibrational quanta, while $H_{02}$ represents the rigid rotor $B_0J(J+1)$, with $B_0$ the rotational quantum number and J the number of rotational quanta. $H_{21}$ represents the Coriolis coupling of the ro-vibrational momenta; $H_{21}$=-$2B_0\zeta(\vec{J}\cdot\vec{l})$ in which $\zeta$ is the Coriolis constant. Higher order terms consist of a combination of terms; they always include tensorial factors. As an example $H_{40}$ is given in eq.2 utilizing the representation of [6].

$$H_{40} = X_{33}v(v-1) + G_{33}[l(l+1) - 2v] + \sqrt{120}T_{33}\hat{T}^{404} \tag{3.2}$$

where $X_{33}$ is the factor responsible for the anharmonic shift of the $\nu_3$ levels.
$G_{33}$ is the factor responsible for the splitting into different l sublevels.
$T_{33}$ is the factor responsible for the splitting of each l sublevel into octahedral sublevels.
$\hat{T}^{abc}$ is a tensor operator with vibrational part of rank a, rotational part of rank b, resulting in a total tensor rank c.

For the two different predictions of the frequencies of the two photon transitions, the same Hamiltonian is used but different representations lead to different expressions for the $H_{ij}$.

In eq.1, the terms left from line 1 are important for the calculations of the frequencies of one photon transitions. With the aid of the commutation relation it is easily shown that the terms right from this line can be left out in the fitting procedure. Higher order perturbation terms, causing processes like $1\nu_3 \leftarrow 2\nu_3 \leftarrow 0\nu_3$ do not change the constants left from line 1 within our experimental accuracy. In the same way it is possible to prove that the terms right from line 2 can be excluded in the calculations of the two photon transitions, the terms right from line 3 have no influence on the prediction of the three photon transitions.

For each Hamiltonian term $H_{(i)}$ an estimate of the order of magnitude of the energy involved is shown; if more components contribute, the largest one is taken into account in this listing. To calculate these energies eq.3 is used in which $E_{nm}$ is the component of the Hamiltonian with vibrational order n, and rotational order m; $C_{nm}$ is a constant taken from table 2 (section 4). To calculate the energies listed in eq.1; v=2 and J=10 are used.

$$E_{nm} = C_{nm}v^n J^m \tag{3.3}$$

In order to predict the two photon transitions within our experimental accuracy of 2 MHz, we need to include all the terms left from line 2 in eq.1. However, the terms marked

with * are estimated to be very small and can be neglected, e g the $H_{45}$ term can be excluded In this way a Hamiltonian including 67 fit parameters can be constructed for the two photon transitions

The terms marked with ⊙ are very small, however, they can not be excluded In the fitting procedure for the one photon transitions as measured by the Bordé group they are important and are determined with very high accuracy [7, 8, 9, 10], this is of great help for the fitting procedure of the two photon transitions The one photon measurements were performed at room temperature, as a result, the rotational population of the molecules extends to much higher J-values than in our measurements where the molecules are cooled

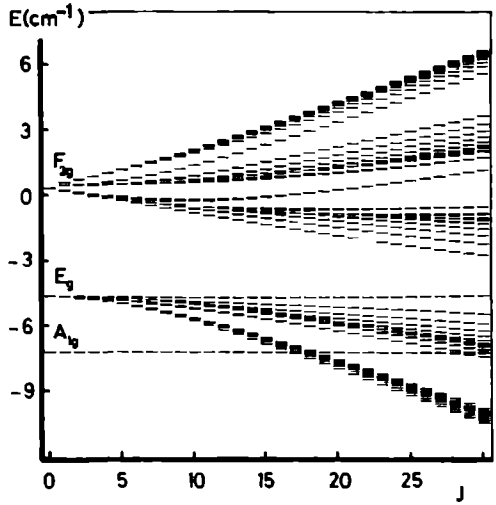


*Figure 1 Energy level diagram for the $2\nu_3$ transitions of $SF_6$ For each J-value up to 30 the relative energy of the different sublevels is plotted The vibrational symmetries of the three branches are indicated, for the $A_{1g}$ symmetry branch l=0, for the $E_g$ and $F_{2g}$ branches l=2*

during the expansion through the nozzle [11, 12] In order to fit these one photon transitions properly, it is necessary to include the terms marked with ⊙, because they will be much larger for higher J-values than the values indicated in the last column of eq 1 For the two photon transitions the predicted energy level scheme is given in fig 1 To fit all the parameters of the Hamiltonian it is necessary to measure transitions with different J-values for all of the symmetry branches For the $A_{1g}$ symmetry (see fig 1) we could not measure and assign two photon transitions, accordingly, the predicted frequencies of this symmetry branch will not

be very accurate (± 200 MHz). On the contrary, we measured many transitions with $\Delta J=0$ and vibrational symmetry $F_{2g}$ so that other transitions of this symmetry type can now be predicted with an accuracy of 3 MHz.

Due to the enormous number of parameters it is sometimes possible to predict a set of transitions with two different sets of parameters. Obviously one of these sets of parameters is not correct. The only way to find out which one is to include more lines in the fitting procedure.

From eq.1 it is clear that in predicting three photon transitions only one extra term, i.e. the $H_{60}$ which contains another 5 extra parameters, has to be included. This will raise the number of parameters which have to be fit to a total of 72. For four photon transitions it is not necessary to include new parameters anymore, they will be predicted with the same set of parameters as the three photon transitions.

## 3.3 Fitting procedure

In [1] a listing of predicted one [13] and two [14, 15] photon transitions, together with the measured frequencies is presented. Numerous measured lines match within 2 MHz with predicted transitions; from this we derived their assignments. However, we did not include our measured two photon transitions in the fitting procedure. The transitions Patterson used for his fit are the one photon transitions measured by the Bordé group in Paris [16], and the two photon transitions presented in [17]. Both measurements are performed in an absorption cell at room temperature; accordingly especially higher J-values where observed. On the contrary, we perform our measurements in a molecular beam in which low rotational energy levels are favoured. Another difference is the use of Acousto Optic Modulators to extend the tuning range of the lasers; in this way many new transitions could be measured and included in the fitting procedure.

In assigning the experimental data, doublets and triplets of transitions starting from the same level, with the same $\Delta J$, are very important. If they are saturated, their intensity depends entirely on their ro-vibrational symmetry ($A_1$:$A_2$:E:$F_1$:$F_2$=1:5:4:3:3) [19]; the distance between the transitions in such a group is fixed within ± 10%. Transitions with J-values not too far apart from each other, with the same $\Delta J$, can be used in a similar way. Utilizing the Boltzmann plot it is possible to estimate the intensity of a predicted transition with a certain J-value from other already assigned transitions with other J-values.

If, because of the large detuning, a transition is not saturated, the strength factor predicted by theory give a rough indication of the intensities of the transitions in the measured spectra. Especially transitions starting from the same J-value, with the same $\Delta J$ and symmetry but with different counting indices (see e.g. the Q(23) E doublet on the 10P16 $CO_2$ laser line, shifted -39 MHz from the $CO_2$ line centre, table 1) sometimes are not predicted with the same relative strength factors $S_S$ and $S_P$. From this and similar multiplets only

the transition with the highest intensity factor is used in the fitting procedure.

Transitions not belonging to a multiplet can only be used in the fitting procedure if they are strong and measured in a frequency region where no other strong unassigned spectral features are observed.

Starting with the transitions measured by the Bordé group [16] and Herlemont et al [14, 18] (in a first attempt to fit our data) resonable agreement is found for the P and Q transitions with $F_{2g}$ vibrational symmetry on the 10P16 $CO_2$ laser line. This is due to the fact that many of these lines are also measured by Herlemont et al, and had thus been already included in the fitting procedure. For the other vibrational symmetries there was often only very poor agreement between the calculated and measured transition frequencies; this is due to the fact that there were almost no transitions of this symmetry which could be assigned before. In order to fit the transitions possessing these symmetries it is often necessary to put into the fitting procedure measured frequencies which are shifted more than 100 MHz from the predicted frequencies.

## 3.4 Results of the fitting procedure

The results of the fitting procedure are given in table 1, in which the measured and calculated transitions are listed, and table 2, in which the constants used to calculate the frequencies of table 1 are listed. In column 2 of table 1, the transitions are listed with their ro-vibrational symmetries. The vibrational symmetries are listed in column 3, being meaningful only for transitions starting from J-values up to approximately 20. For higher J-values strong mixing between the different vibrational symmetries occurs; this mixing of symmetries is responsible for shifts of the energy levels (see fig.1). Especially mixing with transitions possessing $A_{1g}$ vibrational symmetry give rise to high uncertainties in the predicted frequencies because there are not yet many transitions measured with this symmetry. Transitions marked with • are used in the fitting procedure.

In columns 5 and 6 the theoretically predicted two photon transition frequencies of the co-authers B.G. Sartakov and G. Pierre, respectively, are listed. Their strength factors are shown in column 4 and 7. The strength factors are calculated utilizing formula 4.

$$S = I(J)\varepsilon_s \left(\sum \frac{a_{01}a_{12}}{\Delta}\right)^2 \tag{3.4}$$

*I(J)* is a factor depending on the population of the rotational energy levels, derived from the Boltzmann plot as presented in [1]; $\varepsilon_s$ is the ro-vibrational symmetry factor ($A_1$:$A_2$:E:$F_1$:$F_2$=1:5:4:3:3); $a_{01}$ and $a_{12}$ are the dipole transition moments between the initial and intermediate and the intermediate and final levels, respectively; $\Delta$ is the detuning of the laser frequency with respect to the intermediate level. In the calculation of the strength of a transition, all the possible pathways have been included, accordingly, the sum being taken over all possible intermediate levels.

Some transitions are listed with either $\nu_S$ or $\nu_P$; this does not mean that these transitions are not predicted in the other listing. In order to make the listing of calculated transitions not too long, the transitions with strength factors so low that they are not expected to be observable in our spectra, are excluded. Due to the fact that in both calculation other conventions are utilized for the dipole transition moments $a_{01}$ and $a_{12}$, the two predicted strength factors differ approximately by two orders of magnitude. For $\nu_S$ strength factors smaller than 0.1 and for $\nu_P$ strength factors smaller then 10 are left out. Often transitions possessing a low intensity factor $\nu_P$ have an intensity factor $\nu_S$ smaller than .1 and consequently have been excluded from the table.

In column 8 the experimental frequencies of the transitions are listed. Transitions for which it is not possible to find spectral features in the spectra which can be used in an assignment, are marked by a $\star$. Sometimes $\nu_S$ and $\nu_P$ are not the same and differ so much that it is not clear which calculated transition has to be used in the assignment. But more often both predicted frequencies can be used to find the assignment. For the multiplets starting from the same J-value with the same $\Delta$J and symmetry, mostly one of the transitions is much stronger than the other ones. It is not possible to assign the weaker transitions in such a multiplet because either they are too weak to be observed or they are too close to the transition with high intensity to be resolved within our experimental resolution.

For the transitions around the 10P16 $CO_2$ laser line there is not much difference between the predicted frequencies $\nu_S$ and $\nu_P$; also the measured frequencies match within 3 MHz the theoretically predicted values. Three discrepancies between the two calculations and the experimental values still occur. First, the transitions possessing $A_1$ ro-vibrational symmetry have a relatively much stronger $S_P$ than $S_S$ factor. Because the Q(24) transition 190 MHz shifted from the 10P16 $CO_2$ laser line center can be observed in the spectrum, the strength factor as proposed in $S_P$ seems to be alright. Second, the R(38) triplet 250 MHz shifted from the 10P16 $CO_2$ laser line center is estimated much stronger in $S_P$ than in $S_S$. However, in this case measured transition frequencies have not been found to match the predicted values; we conclude that these strength factors are overestimated. The third discrepancy is on transitions possessing $E_g$ vibrational symmetry; they are predicted with low accuracy. Utilizing the two strongest components of the S(19) triplet, it is possible to fix some extra parameters and get the $\nu_S$ and $\nu_P$ in reasonable agreement ($\pm$ 20 MHz) with each other and the experimental data.

For the 10P14 $CO_2$ laser line, only the Q(30) and the R(6) $F_1$ transitions are predicted to possess strong $S_P$ and $S_S$ values. For both transitions it is possible to find measured frequencies which are in good agreement with the predicted ones. For the other transitions, all expected to be weak, the most probable experimental frequency is listed. However their assignment is not certain enough to include these lines in the fitting procedure. Similar arguments hold for the transitions around the 10P20 $CO_2$ laser line.

In order to fit the O-transitions around the 10P18 $CO_2$ laser line, the O(24) triplet is used For the P-transitions in this spectral region, the discrepancy between the two calculated frequencies is very large therefore it is not possible to assign these transitions About the $A_{1g}$ vibrational symmetry only very little is known, this is the reason why the R(16) triplet can not be fitted uniquely

For each term of the Hamiltonian in eq 1, the constants used to predict the frequencies of $\nu_S$ in table 1, are listed in table 2 From this table it can be seen that some of the constants are fit with large accuracy (e g the $Z_{3t}$), while other constants are effectively not fit at all (e g $D_{tvJ}$) In order to fit the set of transitions measured up to now, the terms in the Hamiltonian described by parameters possessing poor accuracies can be excluded However, new experimental data on transitions possessing e g $E_g$ vibrational symmetry cause these parameters to become important Because of the large number of interactions participating in the excitation process of $SF_6$ it is impossible to predict which term of the Hamiltonian is important in the fit of a certain set of transitions Accordingly, if new experimental data are included in the fitting procedure none of the terms of the Hamiltonian can be excluded, it is only afterwards that it can be decided which terms were unimportant

## 3.5 Tables

tabel 1[a]: 10P14 $CO_2$ laser line 28,464,674 MHz

| nr | transitions | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | S(25) $F_1(1)$ | | | | -264 | 56 | -264 |
| 2 | R(20) $F_2(3)$ | $F_{2g}$ | | | -259 | 53 | |
| 3 | Q(34) $F_2(7)$ | | | | -253 | 18 | -257 |
| 3 | Q(30) $F_2(7)$ | | .13 | -233 | -231 | 318 | -233 |
| 4 | Q(30) $F_1(7)$ | | 13 | -230 | -228 | 320 | |
| 5 | Q(34) $F_1(6)$ | | | | -215 | 19 | -212 |
| 6 | R(18) E(1) | $F_{2g}$ | | | -155 | 11 | -152 |
| 7 | R(6) E(1) | $F_{2g}$ | | | -92 | 23 | -94 |
| 8 | R(6) $F_1(1)$ | $F_{2g}$ | 8 10 | -18 | -10 | 60 | -16 |
| 9 | R(6) $A_1(1)$ | $F_{2g}$ | | | 250 | 84 | 247 |
| 10 | Q(14) E(3) | $F_{2g}$ | 12 | 251 | | | 253 |

Tabel 1[b]. 10P16 $CO_2$ laser line 28,412,590 MHz

| nr | transitions | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | Q(23) $F_2(1)$ | $F_{2g}$ | 1 80 | -296 | -296 | 1605 | -298 |
| 2 | Q(23) $F_2(2)$ | $F_{2g}$ | 1 64 | -296 | | | |
| 3 | Q(30) $A_2(1)$ | | 17.58 | -287 | -289 | 1703 | -291 |
| 4 | Q(31) E(1) | | 8.23 | -276 | -278 | 8684 | -277 |
| 5 | Q(27) $A_1(1)$ | | | | -254 | 944 | |
| 6 | P(7) $F_2(1)$ | $F_{2g}$ | 235 00 | -254 | -253 | 1427 | |
| 7• | P(7) $F_2(2)$ | $F_{2g}$ | 671.14 | -254 | -253 | 4010 | -256 |
| 8 | Q(31) $F_1(4)$ | | | | -243 | 11 | |
| 9 | Q(31) $F_1(1)$ | | 2 65 | -238 | -239 | 6720 | -237 |
| 10 | Q(30) $F_2(1)$ | | 2 19 | -237 | -238 | 5302 | |
| 11 | Q(29) $F_2(1)$ | | 2 02 | -226 | -227 | 4200 | -228 |
| 12 | Q(29) $F_2(2)$ | | 2 27 | -226 | | | |
| 13 | Q(25) $F_2(1)$ | | 1 77 | -226 | -226 | 2189 | |
| 14 | Q(26) $F_1(1)$ | | 1.73 | -210 | -209 | 2556 | -210 |
| 15 | Q(28) $F_1(1)$ | | 1.85 | -206 | -206 | 3498 | -205 |
| 16 | Q(30) $F_1(1)$ | | 2 30 | -188 | -190 | 5499 | -191 |
| 17 | Q(30) $F_1(3)$ | | 2.31 | -188 | | | |
| 18 | Q(16) $F_1(1)$ | $F_{2g}$ | 4.13 | -188 | -186 | 1210 | -187 |
| 19 | Q(16) $F_1(2)$ | $F_{2g}$ | 7 37 | -186 | -186 | 121 | |
| 20 | Q(16) $F_1(3)$ | $F_{2g}$ | .43 | -186 | | | |
| 21 | Q(21) $F_1(3)$ | | | | -172 | 12 | |
| 22 | Q(21) $F_1(2)$ | | | | -172 | 17 | |
| 23• | Q(21) $F_1(1)$ | | 2 14 | -171 | -171 | 1480 | -170 |
| 24 | Q(29) E(3) | | | | -166 | 11 | |
| 25 | Q(29) E(2) | | 6.40 | -162 | | | |
| 26 | Q(29) E(1) | | 7 16 | -162 | -163 | 5851 | |
| 27 | P(4) $F_2(1)$ | $F_{2g}$ | 4 $10^6$ | -161 | -162 | 1 $10^6$ | -164 |
| 28• | Q(24) $F_2(1)$ | | 1 75 | -154 | -154 | 1989 | -156 |
| 29• | Q(27) $F_1(1)$ | | 1.74 | -149 | -149 | 3010 | -151 |
| 30 | Q(14) $F_1(3)$ | $F_{2g}$ | 7.03 | -145 | | | |
| 31• | Q(14) $F_1(1)$ | $F_{2g}$ | 5.89 | -145 | -144 | 1146 | -146 |
| 32 | Q(14) $F_1(2)$ | $F_{2g}$ | .26 | -145 | -144 | 50 | |
| 33 | Q(30) $A_1(1)$ | | | | -143 | 1900 | -141 |
| 34• | R(25) $F_2(6)$ | | .29 | -134 | -133 | 375 | -136 |
| 35 | R(25) $F_1(7)$ | | .29 | -132 | -134 | 375 | |
| 36 | Q(28) E(2) | | | | -130 | 10 | |
| 37 | S(20) E(4) | $E_g$ | .28 | -129 | -123 | 78 | * |
| 38 | Q(28) E(1) | | 6 03 | -128 | -128 | 4903 | -127 |
| 39 | S(20) $A_1(2)$ | $E_g$ | | | -123 | 20 | |
| 40 | S(20) $F_1(5)$ | $E_g$ | | | -123 | 59 | |
| 41• | S(19) $A_2(2)$ | $E_g$ | 88 | -107 | -106 | 21 | -107 |
| 42 | Q(29) $F_1(1)$ | | 2 02 | -104 | -104 | 4575 | -103 |
| 43 | S(19) $F_2(4)$ | $E_g$ | 11 | -102 | -100 | 62 | |

Tabel 1[b] (continued)

| nr | transitions | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 44 | S(19) E(3) | $E_g$ | 36 | 99 | 97 | 82 | -98 |
| 45 | Q(26) E(3) | | | | -81 | 14 | |
| 46 | Q(26) E(2) | | | | 79 | 12 | |
| 47 | Q(26) E(1) | | 5 65 | -79 | -78 | 3664 | -79 |
| 48 | Q(25) E(1) | | 5 67 | -76 | 74 | 3165 | -75 |
| 49 | Q(25) E(2) | | 12 | -74 | -76 | 18 | |
| 50 | Q(18) $F_2$(3) | $F_{2g}$ | | | 61 | 22 | |
| 51 | Q(18) $F_2$(2) | $F_{2g}$ | 13 | -60 | -61 | 49 | |
| 52 | Q(18) $F_2$(1) | $F_{2g}$ | 3 27 | -60 | -60 | 1422 | -62 |
| 53• | Q(27) $F_2$(1) | | 1 74 | -53 | -52 | 3193 | -51 |
| 54 | Q(22) E(2) | | | | -51 | 28 | |
| 55 | Q(28) $F_2$(1) | | 1 96 | -52 | 51 | 3867 | |
| 56 | Q(22) E(1) | $F_{2g}$ | 6 07 | -50 | -50 | 2168 | |
| 57 | Q(23) E(2) | $F_{2g}$ | 4 66 | -39 | -39 | 26 | |
| 58 | Q(23) E(1) | $F_{2g}$ | 5 58 | -39 | 38 | 2414 | -38 |
| 59 | S(11) E(2) | $E_g$ | 12 | 21 | | | |
| 60• | Q(11) $F_1$(2) | $F_{2g}$ | 11 59 | 11 | 11 | 1368 | 10 |
| 61 | Q(24) $F_1$(3) | | | | 26 | 13 | |
| 62 | Q(24) $F_1$(1) | | 1 84 | 28 | 28 | 2186 | 25 |
| 63 | Q(26) $F_2$(3) | | | | 31 | 13 | |
| 64 | R(36) $F_1$(5) | | 13 | 31 | 34 | 630 | |
| 65 | Q(26) $F_2$(1) | | 1 82 | 32 | 33 | 2935 | 30 |
| 66 | R(36) $F_2$(6) | | 13 | 36 | 37 | 630 | |
| 67• | Q(27) $A_2$(1) | | 13 74 | 37 | 38 | 1126 | 37 |
| 68 | R(36) $F_2$(3) | | | | 42 | 13 | |
| 69 | Q(19) E(2) | $F_{2g}$ | 22 | 49 | 50 | 50 | |
| 70• | Q(19) E(1) | $F_{2g}$ | 9 61 | 49 | 50 | 2162 | 48 |
| 71 | Q(20) E(3) | $F_{2g}$ | | | 70 | 20 | |
| 72 | Q(20) E(2) | $F_{2g}$ | 26 | 71 | 70 | 66 | |
| 73 | Q(25) $F_1$(4) | | | | 71 | 18 | |
| 74 | Q(20) E(1) | $F_{2g}$ | 8 29 | 71 | 71 | 2342 | 70 |
| 75 | Q(25) $F_1$(1) | | 1 77 | 73 | 73 | 2574 | 72 |
| 76 | Q(21) $F_2$(3) | $F_{2g}$ | | | 141 | 18 | |
| 77 | Q(21) $F_2$(2) | $F_{2g}$ | | | 142 | 17 | |
| 78• | Q(21) $F_2$(1) | $F_{2g}$ | 2 15 | 142 | 143 | 1717 | 142 |
| 79 | Q(23) $F_1$(3) | | | | 152 | 20 | |
| 80 | Q(23) $F_1$(1) | | 1 82 | 153 | 153 | 2002 | 152 |
| 81 | Q(9) E(1) | $F_{2g}$ | 145 14 | 172 | 172 | 2033 | |
| 82• | P(4) E(1) | $F_{2g}$ | $3\,10^7$ | 175 | 174 | $8\,10^7$ | 174 |
| 83 | Q(24) $A_1$(1) | | | | 190 | 796 | 192 |
| 84 | Q(22) $F_2$(4) | $F_{2g}$ | | | 214 | 21 | |
| 85 | Q(22) $F_2$(1) | $F_{2g}$ | 1 95 | 215 | 215 | 1850 | 215 |
| 86 | Q(9) $F_1$(1) | $F_{2g}$ | 29 | 233 | 232 | 68 | |
| 87 | Q(9) $F_1$(2) | $F_{2g}$ | 13 82 | 233 | 232 | 1415 | 235 |
| 88 | R(38) $F_1$(7) | | | | 253 | 643 | * |
| 89 | R(38) $F_2$(8) | | | | 256 | 643 | * |
| 90 | R(38) $F_1$(4) | | | | 264 | 24 | * |
| 91 | P(7) $F_1$(1) | $F_{2g}$ | 18 71 | 266 | 268 | 42 | |
| 92 | P(7) $F_1$(2) | $F_{2g}$ | 905 11 | 266 | 268 | 2159 | 265 |

Tabel 1[c]. 10P18 $CO_2$ laser line 28,359,774 MHz

| nr | transitions | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | 0(26) E(2) | | 79 | -305 | -300 | 413 | -297 |
| 2 | 0(26) E(3) | | 88 | -305 | | | |
| 3 | 0(26) E(4) | | 1 01 | -305 | | | |
| 4 | P(37) $F_2$(4) | | 11 | -270 | -312 | 474 | ⋆ |
| 5 | P(39) $F_2$(5) | | | | -290 | 168 | ⋆ |
| 6 | P(35) $F_1$(4) | | | | -268 | 22 | ⋆ |
| 7 | P(35) $F_1$(3) | | 46 | -234 | -267 | 2538 | ⋆ |
| 8 | O(26) $F_2$(2) | | 25 | -212 | -207 | 313 | -207 |
| 9 | O(26) $F_2$(3) | | 29 | -212 | | | |
| 10 | O(26) $F_2$(4) | | 33 | -212 | | | |
| 11 | O(11) $A_2$(1) | $F_{2g}$ | 57 | -167 | | | -168 |
| 12• | O(24) E(3) | | 66 | -131 | -131 | 259 | -134 |
| 13• | O(24) $F_2$(5) | | 21 | -126 | -126 | 194 | -127 |
| 14• | O(24) $A_2$(2) | | 1 59 | -117 | -117 | 65 | -117 |
| 15 | P(39) $F_1$(6) | | | | -78 | 160 | ⋆ |
| 16 | P(36) $A_1$(2) | | | | 54 | 234 | ⋆ |
| 17 | P(35) $A_1$(1) | | | | 92 | 674 | ⋆ |
| 18 | P(19) $A_2$(1) | $F_{2g}$ | 35 | 113 | | | 113 |
| 19 | R(16) $F_1$(1) | $A_{1g}$+$E_g$ | 78 20 | 125 | | | ⋆ |
| 20 | R(16) $F_2$(1) | $A_{1g}$+$E_g$ | 78 23 | 129 | | | ⋆ |
| 21 | R(16) $F_2$(2) | $A_{1g}$+$E_g$ | 98 52 | 130 | | | ⋆ |
| 22 | P(32) $F_2$(5) | | | | 152 | 42 | ⋆ |
| 23 | P(32) $F_2$(4) | | | | 154 | 14 | ⋆ |
| 24 | P(32) $F_2$(2) | | 1 92 | 179 | 156 | 7199 | ⋆ |
| 25 | P(32) E(4) | | | | 233 | 22 | ⋆ |
| 26 | P(32) E(3) | | | | 236 | 52 | ⋆ |
| 27 | P(32) E(2) | | 6 44 | 261 | 238 | 10419 | ⋆ |
| 28 | O(20) $A_1$(2) | $F_{2g}$ | | | 281 | 42 | |
| 29 | O(20) $F_1$(5) | $F_{2g}$ | 28 | 288 | 281 | 125 | |
| 30 | O(20) E(4) | $F_{2g}$ | 86 | 289 | 282 | 166 | 284 |

Tabel 1[d] 10P20 $CO_2$ laser line 28,306,225 MHz

| nr | transitions | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u. | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | Q(38) $F_2$(6) | | | | -77 | 19 | -74 |
| 2 | Q(38) $F_1$(6) | | | | -48 | 19 | -46 |
| 3 | Q(39) $F_1$(7) | | | | 146 | 30 | 149 |
| 4 | Q(39) $F_2$(7) | | | | 150 | 30 | |
| 5 | O(8) $F_2$(2) | $E_g$ | 21 | 218 | | | 223 |
| 6 | Q(40) $F_2$(8) | | | | 304 | 43 | 308 |
| 7 | Q(40) $F_1$(8) | | | | 305 | 43 | |

*Table 1: Calculated and measured $2\nu_3$ transitions of $SF_6$. The assignment of the transitions with ro-vibrational symmetry is given in column 2. Column 3 contains the vibrational symmetries of the transitions. It is not possible to assign the vibrational symmetries of transitions with J-values higher than 20, because for these transitions there will be mixing of states of different symmetries which influences strongly the energy levels and thus the transition frequencies. In column 5 and 6 the transition frequencies resulting from the two different calculations are listed, the strength factors are listed in column 4 and 7, respectively. The frequency of the experimental lines are listed in column 8. Only the transitions marked with • are used in the fitting procedure. Transitions which are not yet satisfactorily assigned and fit or for which the two calculations predict a largely different frequency are marked by ⋆.*

| | | | |
|---|---|---|---|
| $H_{20}$: | $F_{01}$ | $=948.102509$ | $\pm 1\cdot10^{-6}$ |
| $H_{02}$: | $B_0$ | $=9.10771\cdot10^{-2}$ | $\pm 7\cdot10^{-7}$ |
| $H_{21}$: | $2B_0\zeta$ | $=1.26128\cdot10^{-1}$ | $\pm 1\cdot10^{-6}$ |
| $H_{04}$: | $D_s$ | $=-7\cdot10^{-9}$ | $\pm 1\cdot10^{-9}$ |
| | $D_t$ | $=1.54\cdot10^{-10}$ | $\pm 3\cdot10^{-12}$ |
| $H_{22}$: | $Y_3$ | $=-1.31056\cdot10^{-4}$ | $\pm 8\cdot10^{-9}$ |
| | $Z_{3s}$ | $=9.1747\cdot10^{-5}$ | $\pm 5\cdot10^{-9}$ |
| | $Z_{3t}$ | $=3.75466\cdot10^{-5}$ | $\pm 1\cdot10^{-10}$ |
| $H_{40}$: | $X_{33}$ | $=-1.7467$ | $\pm 1\cdot10^{-4}$ |
| | $G_{33}$ | $=9.2532\cdot10^{-1}$ | $\pm 1\cdot10^{-5}$ |
| | $T_{33}$ | $=-2.4896\cdot10^{-1}$ | $\pm 1\cdot10^{-5}$ |
| $H_{23}$: | $F_{3s}$ | $=3.9\cdot10^{-8}$ | $\pm 5\cdot10^{-9}$ |
| | $F_{3t}$ | $=-1.63\cdot10^{-9}$ | $\pm 1\cdot10^{-11}$ |
| $H_{41}$: | $M_{33}$ | $=1.39\cdot10^{-4}$ | $\pm 1\cdot10^{-6}$ |
| | $N_{33t}$ | $=1.38\cdot10^{-5}$ | $\pm 8\cdot10^{-7}$ |
| $H_{06}$: | $\pi$ | $=-1\cdot10^{-13}$ | $\pm 5\cdot10^{-13}$ |
| | $\rho$ | $=4.8\cdot10^{-14}$ | $\pm 1\cdot10^{-15}$ |
| | $\xi$ | $=1.0\cdot10^{-16}$ | $\pm 2\cdot10^{-17}$ |
| $H_{24}$: | $\Delta D_s$ | $=-4.8\cdot10^{-11}$ | $\pm 7\cdot10^{-12}$ |
| | $\Delta D_t$ | $=8.1\cdot10^{-12}$ | $\pm 2\cdot10^{-13}$ |
| | $\Delta Z_{3sj}$ | $=4.7\cdot10^{-11}$ | $\pm 6\cdot10^{-12}$ |
| | $\Delta Z_{3tj}$ | $=3.28\cdot10^{-12}$ | $\pm 9\cdot10^{-14}$ |
| | $T_{246}$ | $=7.21\cdot10^{-12}$ | $\pm 6\cdot10^{-14}$ |
| $H_{42}$: | $\Delta Y_{3v}$ | $=-2.6\cdot10^{-7}$ | $\pm 5\cdot10^{-8}$ |
| | $\Delta Y_{3l}$ | $=-2.9\cdot10^{-7}$ | $\pm 4\cdot10^{-8}$ |
| | $\Delta Z_{3s}$ | $=2.1\cdot10^{-6}$ | $\pm 3\cdot10^{-7}$ |
| | $\Delta Z_{3t}$ | $=-1.4\cdot10^{-7}$ | $\pm 5\cdot10^{-8}$ |
| | $T_{l220}$ | $=-1\cdot10^{-7}$ | $\pm 2\cdot10^{-7}$ |
| | $T_{l224}$ | $=-1.9\cdot10^{-7}$ | $\pm 2\cdot10^{-8}$ |
| | $\Delta T_{33j}$ | $=3.7\cdot10^{-7}$ | $\pm 2\cdot10^{-8}$ |
| | $T_{426}$ | $=-2.7\cdot10^{-7}$ | $\pm 1\cdot10^{-8}$ |
| $H_{25}$: | $a_5$ | $=6\cdot10^{-13}$ | $\pm 2\cdot10^{-12}$ |
| | $b_5$ | $=-2.57\cdot10^{-13}$ | $\pm 5\cdot10^{-15}$ |
| | $d_5$ | $=-1.05\cdot10^{-14}$ | $\pm 5\cdot10^{-16}$ |
| $H_{43}$: | $M_{33j}$ | $=-1.4\cdot10^{-8}$ | $\pm 3\cdot10^{-9}$ |
| | $N_{33tj}$ | $=-7\cdot10^{-9}$ | $\pm 2\cdot10^{-9}$ |
| | $F_{3tv}$ | $=6\cdot10^{-10}$ | $\pm 8\cdot10^{-10}$ |
| | $T_{336}$ | $=-1.4\cdot10^{-8}$ | $\pm 1\cdot10^{-9}$ |
| $H_{08}$: | $D_{sjj}$ | $=7\cdot10^{-19}$ | $\pm 2\cdot10^{-17}$ |
| | $D_{tjj}$ | $=3.4\cdot10^{-18}$ | $\pm 3\cdot10^{-19}$ |
| | $\xi_j$ | $=1\cdot10^{-21}$ | $\pm 3\cdot10^{-20}$ |
| | $H_{08}$ | $=4\cdot10^{-17}$ | $\pm 5\cdot10^{-17}$ |
| $H_{26}$: | $X_{vjjj}$ | $=-1.2\cdot10^{-15}$ | $\pm 4\cdot10^{-16}$ |
| | $Z_{3sjj}$ | $=2.1\cdot10^{-15}$ | $\pm 4\cdot10^{-16}$ |
| | $Z_{3tjj}$ | $=-1.4\cdot10^{-16}$ | $\pm 1\cdot10^{-17}$ |
| | $D_{tvj}$ | $=5.58\cdot10^{-16}$ | $\pm 4\cdot10^{-18}$ |
| | $\xi_v$ | $=1.01\cdot10^{-17}$ | $\pm 2\cdot10^{-19}$ |
| | $T_{246j}$ | $=-3.2\cdot10^{-16}$ | $\pm 2\cdot10^{-17}$ |
| | $T_{268}$ | $=1.7\cdot10^{-14}$ | $\pm 1\cdot10^{-15}$ |
| $H_{44}$: | $X_{33jj}$ | $=1.4\cdot10^{-10}$ | $\pm 4\cdot10^{-11}$ |
| | $G_{33jj}$ | $=-4\cdot10^{-11}$ | $\pm 2\cdot10^{-11}$ |
| | $T_{33jj}$ | $=-8\cdot10^{-11}$ | $\pm 1\cdot10^{-11}$ |
| | $Z_{3svj}$ | $=-9\cdot10^{-10}$ | $\pm 2\cdot10^{-10}$ |
| | $Z_{3slj}$ | $=-1\cdot10^{-10}$ | $\pm 1\cdot10^{-10}$ |
| | $Z_{3tvj}$ | $=-2\cdot10^{-12}$ | $\pm 4\cdot10^{-11}$ |
| | $Z_{3tlj}$ | $=3\cdot10^{-11}$ | $\pm 2\cdot10^{-11}$ |
| | $T_{246v}$ | $=7.3\cdot10^{-11}$ | $\pm 8\cdot10^{-12}$ |
| | $T_{246l}$ | $=1.4\cdot10^{-11}$ | $\pm 6\cdot10^{-12}$ |
| | $T_{426j}$ | $=1.1\cdot10^{-10}$ | $\pm 3\cdot10^{-11}$ |
| | $T_{440}$ | $=2\cdot10^{-10}$ | $\pm 1\cdot10^{-10}$ |
| | $T_{448}$ | $=-2.3\cdot10^{-8}$ | $\pm 2\cdot10^{-9}$ |
| | $D_{tvv}$ | $=3.2\cdot10^{-11}$ | $\pm 6\cdot10^{-12}$ |
| | $D_{tll}$ | $=2.2\cdot10^{-11}$ | $\pm 4\cdot10^{-12}$ |
| $H_{27}$: | $a_{5j}$ | $=2\cdot10^{-18}$ | $\pm 7\cdot10^{-17}$ |
| | $b_{5j}$ | $=8.9\cdot10^{-18}$ | $\pm 9\cdot10^{-19}$ |
| | $d_{5j}$ | $=-3\cdot10^{-19}$ | $\pm 9\cdot10^{-19}$ |
| | $e_7$ | $=3\cdot10^{-16}$ | $\pm 4\cdot10^{-16}$ |

*Table 2: Constants utilized in the Hamiltonian (equation 1) to predict the frequencies $\nu_S$ in table 1. The constants are ordered according to the terms of the Hamiltonian in which they participate.*

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Chapter 4

# Multiphoton experiments on $SF_6$, molecular quantum electronics with infrared radiation

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## Abstract

Multiphoton experiments on $SF_6$ in a molecular beam are performed utilizing cw $CO_2$ waveguide lasers. In this paper the emphasis will be on the non-spectroscopic aspects. -The saturation dip in one photon transitions is measured. -To investigate which rotational states participate in the multiphoton process, an intra cavity laser is used as a pump laser, followed by a waveguide laser. Only hot band transitions seem to be depleted. -With the aid of two counter propagating $CO_2$ waveguide laser beams, new spectral regions were entered to investigate two photon transitions. In this way it is also possible to investigate three and more photon transitions, because of the higher intensity (two lasers) and smaller intermediate detunings (two colours).

## 4.1 Introduction

Since a few years the possibility of introducing rapid adiabatic processes (RAP) in spectroscopic and collision studies has been exploited by the Nijmegen group [1-6]. There are at least two ways to realize RAP. Either a (linear) frequency chirp is applied, a method useful for one colour $1h\nu$ or $nh\nu$ transitions, or, in case of two or more colour excitation, a counter intuitive sequence of laser interactions is introduced [7-12], i.e. in a pump-probe experiment the probe laser comes first followed by the pump laser with temporal (in our case of a molecular beam, partial spatial) overlap [4].

In this paper results obtained for $SF_6$ are discussed. The emphasis will be on the non-spectroscopic aspects of the investigations; under RAP-conditions, the absence of saturation broadening, in general (and specifically for $1h\nu$ saturation dips) and measurements of two and more photon transitions utilising two different lasers will be discussed. In section 2

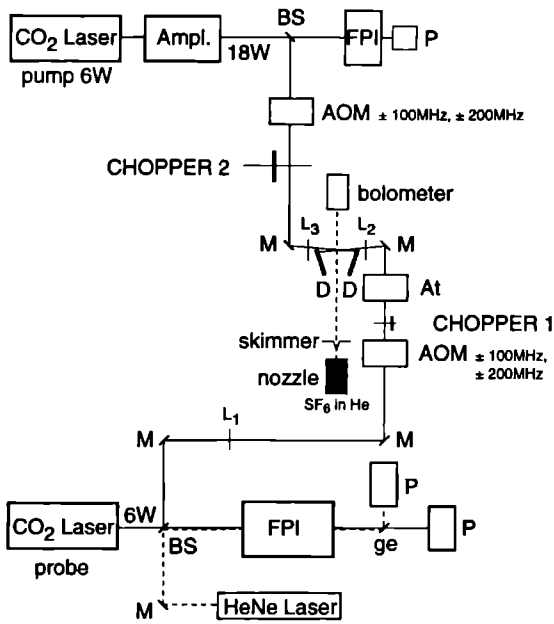


*Figure 1: Experimental set-up. BS, beam splitter (R=90cm); M, flat mirror; AOM, Acousto Optic Modulator; P, power meter; FPI, Fabry-Perot interferometer; ge, germanium plate; D beam dumps; ampl, $CO_2$ amplifier; At, attenuator.*

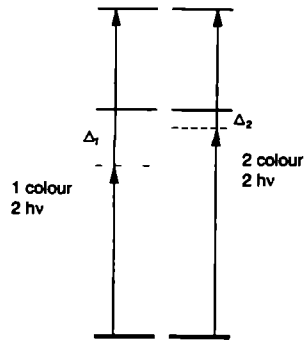


*Figure 2 The intermediate detuning of a two photon transition can be reduced, utilizing two colour instead of one colour excitation*

the experimental set-up will be described briefly Depletion measurements utilizing an intra cavity laser as a pump and a wave guide laser as a probe laser are discussed in section 3 In section 4 two level systems, in section 5 three level systems and in section 6 four and more level systems are considered

## 4.2 Experimental set-up

The experimental set-up used in the present experiments has been described before [6] There are two new aspects From the point of view of laser interactions we realized two colour fields, where two single mode laser fields interact simultaneously with the $SF_6$ molecules of a molecular beam The realization of this concept is not a trivial task because we work with cw $CO_2$ waveguide lasers, in most experiments this radiation is focused to a waist of 0 1 mm diameter in order to obtain enough laser fluence (laser power × time of flight of molecules through the laser field) to induce multiphoton effects

We work with two counterpropagating laser beams - both orthogonal to the molecular beam axis - just inclined so little that they do not disturb the well functioning of the opposite laser (see fig 1) The alignment is facilitated by the observation of intense two colour multiphoton excitations One laser is fixed in frequency and chopped, whereas the second laser is not chopped but scanned in frequency Thus transitions are produced and observed as a result of the combined action of both lasers The simultaneous character makes it possible to cope with transitions where large detuning $\Delta$ occurs for the intermediate level(s) First the use of two different colours can decrease the intermediate detuning (see

fig.2) and secondly the radiation intensity is increased by a factor 2, allowing a larger detuning. Since e.g. the $2h\nu$ Rabi frequency goes linearly with $\Delta^{-1} \times P_{laser}$ both effects contribute to render a relatively weak transition observable.

It is evident that the simultaneous presence of two colour laser fields opens new spectral regions for the final states, very similar to what has been postulated and realized in earlier low resolution experiments employing pulsed lasers in multiphoton excitation of molecules [13, 14]. In the present experiment we exploit the about 1 MHz resolution of our cw lasers (tunable over about ± 125 MHz around the strong $CO_2$ laser transitions) to obtain one, two and three photon excitation spectra with 2 MHz resolution.

A second new aspect of our experimental set-up is the installation of $CO_2$ waveguide amplifiers, instead of the conventional amplifier used in [6]. This permits us to obtain amplification over the full tuning range of the laser oscillator, with a maximum power of 25 W. Other advantages are a reduction of coupling losses and conservation of the $TEM_{00}$ mode.

We use Acousto Optic Modulators (AOM's) to increase the tuning range above ±125 MHz, in steps of 100 MHz per passage around the fundamental laser transition. We loose about a factor of 2 in laser power per passage. Using two sideband shifters together with the tuning range of the waveguide laser, allows a total tuning range of 1 GHz around a $CO_2$-transition, with a factor 4 drop in laser power.

To investigate saturation dips in our molecular beam signal, a single laser is retro-reflected and crosses the molecular beam again, so that $SF_6$ molecules travelling parallel to the molecular beam axis have the possibility to interact with the unreflected and reflected laser radiation. In this way the Doppler residue of the molecular beam is eliminated. The FWHM of $1h\nu$ saturation dips is now solely determined by the time of flight broadening (± 500 kHz) and laser stability. It appears that our lasers have a stability better than 500 kHz, during several seconds.

Since we are interested in the consequences of RAP, the minimum waist is mostly chosen to be very narrow (about 0.1 mm diameter) and normally does not coincide with the molecular beam axis. In earlier experiments [6] where we wanted to observe $2h\nu$ Rabi oscillations this coincidence between minimum waist and molecular beam axis was achieved.

## 4.3 Depletion measurements

Two colour excitation has been performed with two in space separated laserfields to investigate depletion effects on single rovibrational states due to a strong pump field. To investigate the participation of various initial states of the $\nu_3$-ladder in the multiphoton process in $SF_6$, we first cross the molecular beam with an intra-cavity laser (300 Watt) set on the 10P24 $CO_2$ laser line, i.e. on maximum multiphoton signal. A few centimeters downstream, we probe the same molecules with a waveguide laser, set on the 10P16 line with

double passage through the AOM Within our experimental accuracy of 10%, we could not detect any depletion of the P(4) two photon transitions (peak A in fig 3), this in contrast with measurements of V M Apatin et al [15], from which we expected depletions up to 30% The measurements of [15] are critically discussed, theoretically [16] On the other hand, the unassigned spectral features (peaks B and C in fig 3), coming probably from hot band transitions, vanish almost completely This and similar findings suggest that thermally excited vibrational states form very effective departure levels for multiphoton excitation

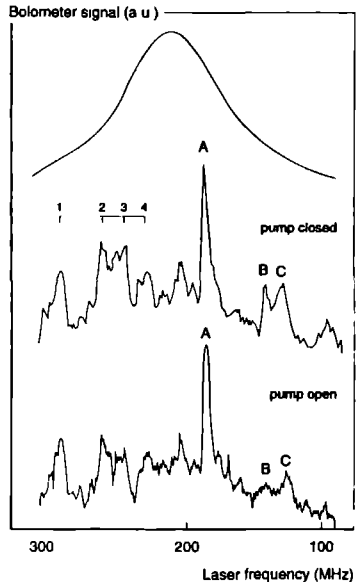


*Figure 3 Pump-probe experiment with an intra cavity laser set on the 10P24 $CO_2$ laser line as a pump laser (300 Watt), and a 200 MHz shifted waveguide laser (1 5 Watt), scanned around the 10P16 $CO_2$ laser line The numbers 1 to 4 mark the position of the P(4) quadruplet, peak A is the P(4)E(0) $2h\nu$ transition and B and C are two not assigned $2h\nu$ hot band transitions When the pump laser is opened, no dramatic changes in the spectrum are observed except for the two hot band transitions B and C, which disappear almost completely*

Excitation of a molecule either from the ground or from a thermally populated vibrational level may yield a very different number of possible transitions due to the difference in selection rules There are well known selection rules $\Delta J=0,\pm 1$, $\Delta R=0$ and $\Delta p=0$ for the fundamental vibrational transition of the $\nu_3$ mode [17] Here R is the rotational angular-momentum quantum number and p the quantum number to assign octahedral sublevels of the same symmetry If we deal with initially already excited vibrational states where strong

R mixing takes place, the selection rules $\Delta R=0$ and $\Delta p=0$ can be violated It is known e g for the $2\nu_3$ transition of $CH_4$ [18] and for the $3\nu_3$ transition of $SF_6$ [19], that these selection rules are violated due to the strong anharmonic coupling of the levels in the excited vibrational state For example, if for $SF_6$ the departure level is $\nu_6$, the selection rule $\Delta R=0$ becomes invalid due to the R mixing in the $\nu_3+\nu_6$ final vibrational state The vibrational degeneration of the $\nu_6$ level is 3, and of the $\nu_3+\nu_6$ level 9 The number of allowed transitions due to $\Delta R\neq 0$ is 9 times larger than for the fundamental $\nu_3$ transition If one takes into account the violation of the $\Delta p=0$ selection rule, this difference is even more enhanced by about a factor of J/2 This great enhancement of allowed transitions makes it relatively easy to find laser coincidences for transitions from thermally populated vibrational levels such like $\nu_6$, $2\nu_6$ and $\nu_5$, which possess low energy and high degeneracy

## 4.4 Two level systems, N=2

Before starting the discussion on the new points we want to draw attention once more to the double resonance experiments which demonstrate the occurrence of RAP inversion through the first laser interaction with $C_2H_4$ molecules in a molecular beam This demonstration is based on the use of a second laser interaction downstream, where the population inversion is undone and stimulated emission occurs, producing a bolometer signal about equally strong as and negative with respect to the absorption signal induced by the first laser interaction alone [1] In the meantime, this experiment has been repeated also for the P(4) one and two photon resonances of $SF_6$ (fig 6 and 10 of [6]) There, too, the reversal of the inversion by stimulated emission has been observed together with the nearly complete absence of power broadening of the RAP signal

On this last issue we want to add new information Theoretically, once the conditions for RAP are established, an increase in laser power does not lead to anything but inversion Experimentally things are slightly different Some power broadening occurs if the laser power is increased about thousand times over the lower limit value needed for complete inversion, but this broadening is 2 orders of magnitude lower than expected from the standard expression for power broadening, i e FWHM $\approx$ Rabi frequency However, concomitantly with this rudimentary power broadening we observe the disappearance of the inversion to a point where the second laser interaction yields a zero effect We thus conclude that by the increase of laser power a 50% population of both levels is achieved, without the effect of residence time broadening due to the increasing Rabi frequency [6] This observation might be explained by the presence of various modes in our laser beam, which, even if they are a hundredfold less intense than the main gaussian mode, finally show up when the power level is increased more than a hundred times

Another experiment was performed utilizing only one laser The laser beam, however, crosses the molecular beam twice at practically the same spot, which induces a saturation

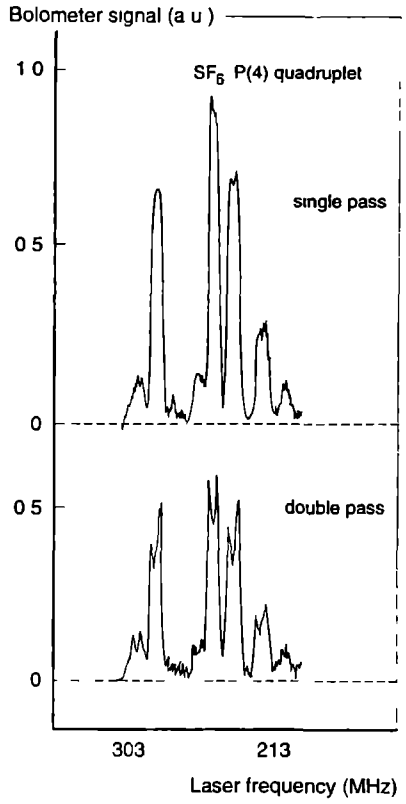


*Figure 4 Saturation dip measurements on the P(4) one photon quadruplet in $SF_6$, upper spectrum taken with single passage of the laser through the molecular beam, lower spectrum taken with double passage, the saturation dips on top of the one photon transitions are clearly visible The width of the dip corresponds to the time-of-flight broadening*

dip (see fig 4) that is caused by the molecules parallel to the molecular beam axis which "see" both laser fields Under normal conditions this saturation dip is known to show power broadening of the order of $\frac{1}{2}\pi \ \Omega_{\mathrm{Rabi}}$ In case of our RAP conditions (i e the laser beam is narrowly focussed both ways, but not precisely on the molecular beam) no broadening of the saturation dip has been found

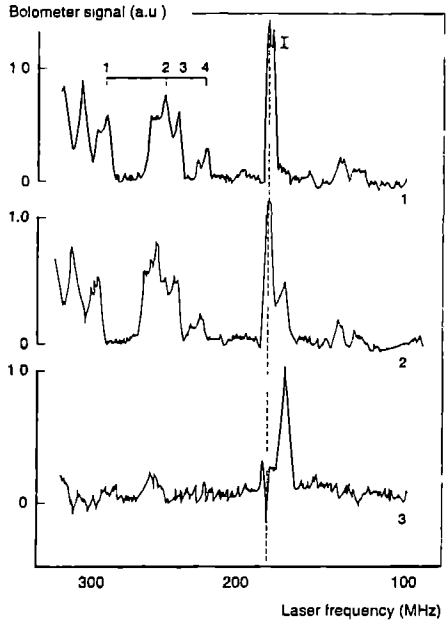


*Figure 5: Pump-probe experiment utilizing two overlapping, counter propagating lasers. In spectrum 1, the chopped probe laser is scanned over the 10P16 $CO_2$ line and shifted 200 MHz (1.5 Watt). I marks the position of the P(4)E(0) $2h\nu$ transition and the numbers 1 to 4 mark the position of the P(4) one photon quadruplet. The unchopped pump laser, fixed on the 10P14 $CO_2$ laser line (18 Watt), is opened and again a spectrum is taken (spectrum 2). The chopper is moved from the probe laser to the pump laser, resulting in spectrum 3, where on top of a continuous background signal caused by the pump laser the spectral features produced by the interaction of the molecules with both lasers simultaneously are recorded.*

## 4.5 Three level system, N=3

In [6], three level systems have been investigated with one colour $2h\nu$ excitation showing many new transitions in $SF_6$, amongst which the P(4)E(0) transition 174 MHz shifted from the 10P16 $CO_2$ line center, with an extraordinarily small detuning of the intermediate level (76 MHz), peak A in fig.3.

We present here our first results on two photon spectroscopy using two coincident counter propagating laser beams. To isolate the two colour signal from the one colour signal we chop

the laser that is fixed in frequency whereas the unchopped (probe) laser is scanned over the full tuning range. Since the bolometer is sensitive only to modulated signals the fixed laser alone will atmost produce a non varying background. If a transition is made involving both laserfields the signal will be modulated due to the contribution of the fixed laser. In this way the spectra can be simplified showing only the $n\hbar\nu$ transitions ($n \geq 2$) resulting from two colour interaction (spectrum 3 of fig.5). In the upper part of figure 5, the -still chopped- probe laser is scanned over the 10P16 $CO_2$ laser line, shifted 200 MHz. Then the pump laser is aligned counter propagating to the probe laser and set on the 10P14 $CO_2$ laser line; spectrum 2 is thus obtained showing both the structure produced by the probe laser and structures caused by both lasers simultaneously. To find the differences in the two spectra, instead of the probe laser, the pump laser is chopped. Now only the differences in spectra one and two are monitored (spectrum 3), which are exactly the structures we are looking for.

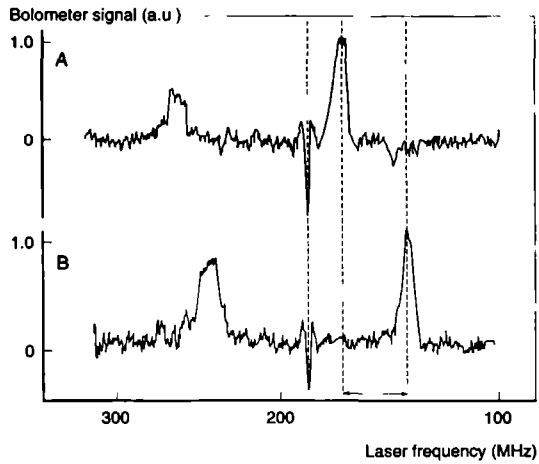


*Figure 6: Spectra taken with two overlapping, counter propagating lasers. The probe laser was scanned around the 10P16 $CO_2$ line and shifted 200 MHz. In A the pump laser is fixed on the 10P14 $CO_2$ line center, the dip coincides with the P(4)E(0) $2h\nu$ transition, the two positive peaks are two photon transitions. If we shift the pump laser approximately 50 MHz to the blue, the two photon transitions have to shift 50 MHz to the red to be on resonance again, see spectrum B.*

To illustrate the dependence of the signal on both laserfields, the frequency fixed laser was displaced to the blue by about 30 MHz. Scanning the probe laser the two colour transition

frequency should shift to the red by the same amount (in case of a two photon transition) This is clearly shown in fig 6, where the pump laser is fixed on the 10P14 $CO_2$ line center (spectrum A) For spectrum B, the pump laser is shifted to the blue by approximately 30 MHz, producing a red shift for $2h\nu$-peaks, with respect to the one-colour $2h\nu$ transition dip For A and B the probe laser is scanned around the 200 MHz shifted 10P16 $CO_2$ laser line The dip coincides exactly with the P(4)E(0) two photon transition in the probe laser scan and is not shifted

In fig 7 a dense spectrum of multiphoton transitions is presented using a strong pump (18 Watts) and a relatively weak (5 Watts) $CO_2$ probe laser, set on the 10P14 and 10P16 $CO_2$ laser transitions, respectively The weak laser is scanned The two strong features we assigned as the $Q(21)F_2$ at 72 MHz and the $Q(17)F_2$ at -46 MIlz two photon transitions Similar spectra have been made for other combinations of $CO_2$ laser lines, showing many new transitions Their assignment is discussed in a separate paper [20]

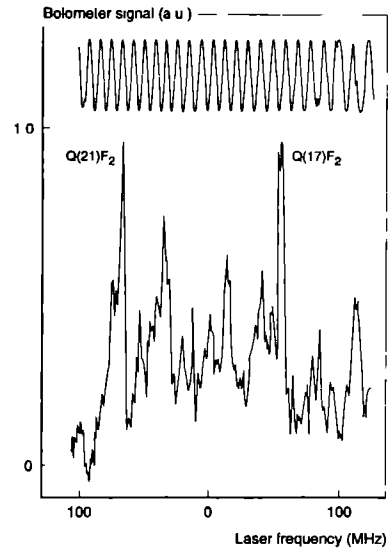


*Figure 7 Two colour spectrum, taken with the pump laser (18 Watt) fixed on the 10P14 $CO_2$ line, the probe laser is scanned around the 10P16 $CO_2$ line (6 Watt) The two assigned transitions are two photon transitions, predicted in theoretical calculations Above the spectrum, the distance between two fringes is 9 MHz*

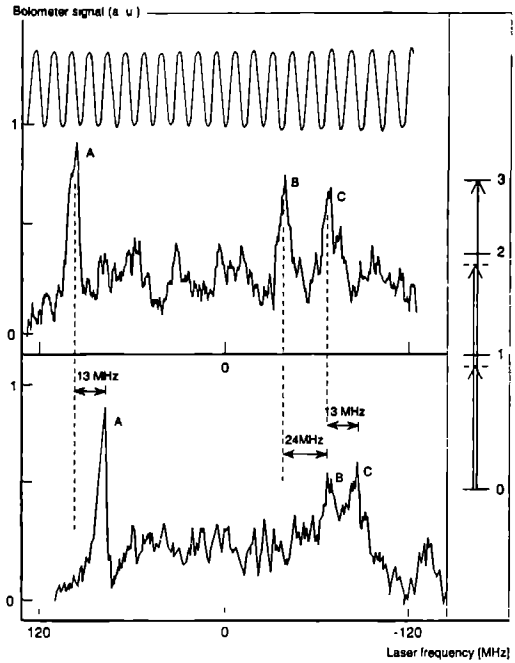


*Figure 8: Spectra taken with the probe laser scanned around the 10P14 $CO_2$ line (5.5 Watt). In the upper spectrum, the pump laser (18 Watt) is set on the 10P16 line center; in the lower spectrum, the pump laser is shifted 13 MHz to the blue. Transitions A and C, assigned as two photon transitions ($Q(21)F_2$ and $Q(17)F_2$, respectively) shifted 13 MHz to the red to compensate for the shift of the pump laser. Transition B, however, shifts twice as fast to the red; thus we deal with a three photon transition, utilizing two photons from the pump and one photon from the probe laser, as indicated in the energy level diagram at the right.*

## 4.6 N> 3 level systems

An interesting phenomena showed up interchanging the role of the two lasers of fig.7. The chopped pump laser at the 10P16 line centre has now an intensity of 18 Watt, the probe laser is scanned around the 10P14 line center, with 5.5 Watt intensity (upper part of fig.8). At -30 $\pm$ 10 MHz detuning a new very strong transition is observed (peak B). Apparently

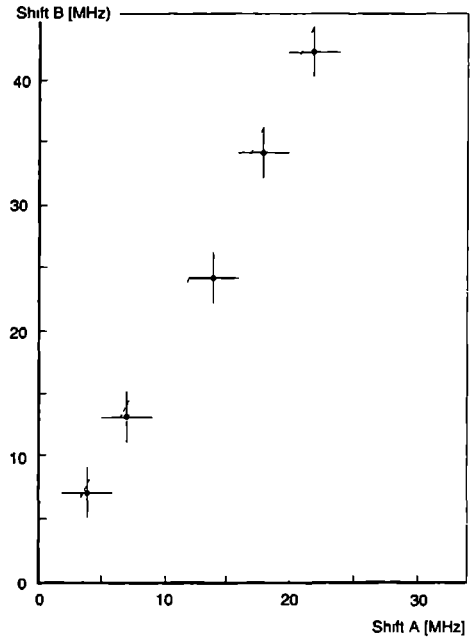


*Figure 9 Shift of transition B, relative to the shift of transition C in figure 8 The dotted line is what is expected for a three photon transition according to the energy level diagram in figure 8, the data fit very well within the experimental accuracy*

one step in the excitation depends strongly on the intensity of the 10P16 laser This fact forms an indication that peak B is due to a ($n h\nu_{10P16}+h\nu_{10P14}$)-type transition with n>1 For n=1, the interchange of laser characteristics would show no big influence as observed for peak A and C In addition the position of peak B does match neither with calculated one nor with two photon frequencies A R(16)E three photon transition of the type ($2h\nu_{10P16}+h\nu_{10P14}$) is predicted almost exactly coinciding with the observed transition B

To prove that we definitely deal here with a three photon transition we shifted the pump laser frequency by varying amounts, each time taking a new spectrum by scanning the probe laser (see e g the lower part of fig 8 where the shift amounts to 13 MHz) Every time the shift of the two photon two colour transitions is measured and compared with the shift of peak B If this peak is due to a three photon transition there are two possibilities, a) either the peak shifts twice as fast as the two photon transitions, indicating that two photons from

the pump laser are needed to make the transition, or b) the peak shifts twice as slowly as the two photon transitions, indicating that only one photon is needed from the pump laser to produce the transition.

In fig.9 the shift of transition B is plotted against the shift of the two photon transitions; the theoretically predicted shift for alternative a) is indicated by the dotted line. From this, we conclude that we really deal here with a three photon transition, utilizing two photons from the pump and one photon from the probe laser, as indicated in the energy level scheme in fig.8.

For N>3 level systems, the experimental possibilities are subject to certain restraints. With one colour excitation of $SF_6$ two things have been shown experimentally. There is a vibrational bottleneck at n=5 (i.e. under RAP conditions inverted populations can be created up to the fifth level of the $\nu_3$ mode; higher up one either runs out of resonance or the high density of states prevents RAP-processes to occur [1]). Furthermore, at this bottleneck level no spectral features have been resolved. This second point might render experiments where the bottleneck is overcome employing two or more colour excitation less interesting, from a spectroscopic point of view.

On the other hand, with one colour excitation and fluences up to 0.01 $J/cm^2$ (typical for our waveguide lasers with an amplifier stage focused to 0.1 mm ø) no three or four photon excitations have been identified. However, with two colour excitation (simultaneous excitation by two overlapping $CO_2$ laser foci) sharp spectral structures due to at least three photon excitation have been found in the present work. This opens the way for new spectroscopy at excitation up to 3000 or even 4000 $cm^{-1}$.

## 4.7 Acknowledgement

We would like to thank Cor Sikkens, Frans van Rijn and John Holtkamp for their permanent and skilful technical assistance. The dutch organisations N.W.O. and S.T.W. made this investigation possible by generous financial support.

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Chapter 5

# Multiphoton multi laser excitation of the $\nu_3$ mode of $SF_6$ in a molecular beam

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## Abstract

Results are presented of measurements utilizing two counter propagating $CO_2$ waveguide lasers interacting simultaneously with $SF_6$ molecules in a molecular beam 95 two photon transitions were observed and assigned, for combinations of two different $CO_2$ laser lines Especially transitions to levels of $E_g$ vibrational symmetry provided new information on the parameters of the Hamiltonian because older one colour measurements could barely access these levels Still no transitions were found to levels with $A_{1g}$ vibrational symmetry Some results are presented on three and four photon transitions

## 5.1 Introduction

Two counterpropagating c.w. $CO_2$ lasers are applied simultaneously to $SF_6$ molecules in a molecular beam. The frequencies can be continuously tuned over $\pm$ 500 MHz. With this technique it is possible to enter new spectral regions at about 10 $\mu$m. Many new transitions are measured which allow to fit the $SF_6$ Hamiltonian.

These new lines lead to a better understanding of the Hamiltonian of $SF_6$. Previously, the group of Bordé [1, 2] has determined 310 one photon transitions with extremely high accuracy. The restriction to levels at about 1000 $cm^{-1}$ is compensated by the small value of the FWHM, 3 kHz. The initially populated and measurable levels possess rotational quantum numbers $12 \leq J \leq 95$, since the measurements were performed at room temperature.

In addition, Herlemont et al [3, 4] observed two photon transitions by saturation spectroscopy (FWHM 200 kHz, room temperature measurements). Both these series of measurements form the basis of the determination of the parameters in the $SF_6$ Hamiltonian by G. Pierre who resently also included many transitions observed by us; these new measurements are reported in [5] (two photon one colour (TPOC) spectra) and in this work (two photon two colour (TPTC) spectra). Independently, and using a slightly different but in principal equivalent form of the $SF_6$ Hamiltonian [6] the other co-author of this paper, B.G. Sartakov, bases predictions of transitions on older work of the group of Bordé, and the here presented TPTC spectra.

The measurements were extended to the 3000 $cm^{-1}$ region; even the first observation of four photon transitions are reported below. Already in 1980 A.S. Pine et al [7, 8] reported $3h\nu_3$ overtone measurements for $SF_6$, observed in a molecular jet, $5 \leq J \leq 35$. These measurements possess linewidth of 30 MHz and are not taken into account in the fits presented in this paper. They agree within their linewidth with Sartakov's calculated values.

In section 2, the experimental set-up as well as some tricks to determine the frequencies of the multiphoton transitions are presented. The experiments aim at the observation of discrete multiphoton transitions with MHz resolution. It is well known that e.g. with pulsed lasers, but also with c.w. lasers interacting with vibrationally hot $SF_6$ molecules, unstructured background-like multiphoton excitation has been observed [9]. In section 3, the interaction by a c.w. 150 Watt $CO_2$ laser (Apollo, Sales Laser Photonics, Carlsbad U.S.A.) is described. The laser is not fine tuned, but set to the maximum of different $CO_2$ laser transitions. Especially for the 10P24 transition, depletion measurements are discussed which demonstrate that only the already thermally excited energy levels are depleted. Transitions starting from the ground state level of $SF_6$ show no signal decrease by the interaction with the Apollo laser; accordingly we conclude that the molecules in the ground state of $SF_6$ barely participate in the background-like multiphoton process.

Our interest is directed towards multiphoton transitions. Therefore, possible power broadening forms an interesting issue. Note that normally we work with laser powers up to

600 times larger than what is needed for complete saturation of one photon transitions. To clarify the saturation issue, the Apollo laser has been employed (possessing even 6000 times the intensity needed for saturation) to investigate power broadening effects of the assigned two photon transitions; no power broadening is observed, the results are discussed in section 4.

In section 5, dynamical Stark effects as observed in the spectra are discussed. These Stark effects are produced by the interaction of the pump laser with the levels of transitions in resonance with the probe laser. This probe laser is not chopped; accordingly transitions induced by the interaction of molecules with the probe laser only should not be observed in the spectra. For the strong one photon transitions (P(4) quadruplet on the 10P16 $CO_2$ laser line) and two photon transitions (P(4) doublet on the 10P16 $CO_2$ laser line), the dynamical Stark effect is observed very clearly and renders the probe laser transitions observable.

The assigned TPTC transitions are presented in section 6. Preliminary results on three and four photon transitions are presented in section 7. Some concluding remarks and suggestions are made in section 8: the outlook.

## 5.2 Experimental set-up

The experimental set-up is described in detail in [5, 6, 9, 10]; there are two new aspects. To investigate power broadening effects of the transitions and depletion of hot band transitions, high intensities are required. In order to achieve this, a commercially available Apollo laser is installed. This laser produces 150 W outcoupled power in a $TEM_{00}$ mode, on the strong 10P lines. This in contrast with the intra-cavity laser utilized in [5], which produces twice as much power with, however, rather poor beam qualities.

A second new aspect is the installation of a Lamb dip cell [11, 12]. In the two laser experiments, performed to investigate two and more photon transitions, the pump laser is fixed in frequency. To determine the distance between two transitions in a spectrum, it is necessary to keep the pump laser frequency fixed for more than 10 minutes, i.e. the time needed to scan the second laser (probe laser) over it's total tuning range of 230 MHz. In order to do so, the pump laser is locked to the dip in fluoresence signal of a Lamb dip cell [13].

The rotational cooling of the molecules during the expansion through the nozzle is very sensitive on the stagnation pressure behind the 50 $\mu$m nozzle [14, 15], as can be seen in fig.1. In fig.1, spectra taken with only one laser are shown with a background pressure of 300 Torr (upper spectrum) and 700 Torr (lower spectrum). All assigned two photon transitions are marked. Especially the Q(29) transition left in the spectra is difficult to find back in the lower spectrum. The Q(29) transition is a strong one [6]; with the laser intensities utilized to produce this spectrum, it is saturated. Its vanishing is caused by the depletion of the J=29 rotational energy level due to the better cooling of the molecules in the expansion.

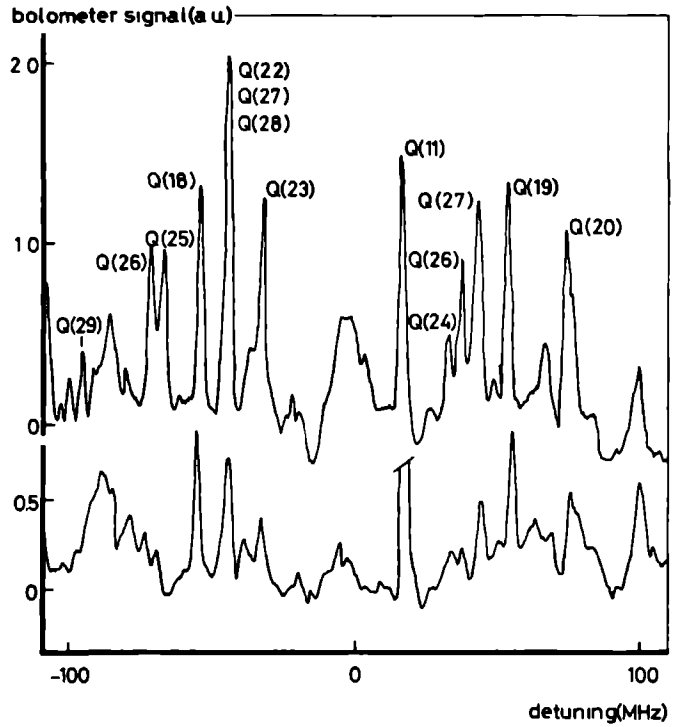


*Figure 1 Dependence of the intensity of the measured two photon transitions on the 10P16 $CO_2$ laser line on the stagnation pressure behind the 50 $\mu$m nozzle The upper spectrum is taken with 300 Torr stagnation pressure, the lower spectrum with 700 Torr resulting in a much better rotational cooling In the lower spectrum the transitions starting from low J-values are relatively much higher than the transitions starting from higher J-values In the assignment of the transitions, the dependence on the background signal is very usefull*

To find transitions starting from high J-values with low strength factors, it is important to take the spectra with lower background pressure On the contrary, transitions starting from energy levels with low J-values, 700 Torr background pressure leads to optimum signals

The measured spectral region can be covered in several ways choosing the right $CO_2$ laser line combination and configuration of Acousto Optic Modulators (AOM's) The AOM's shift

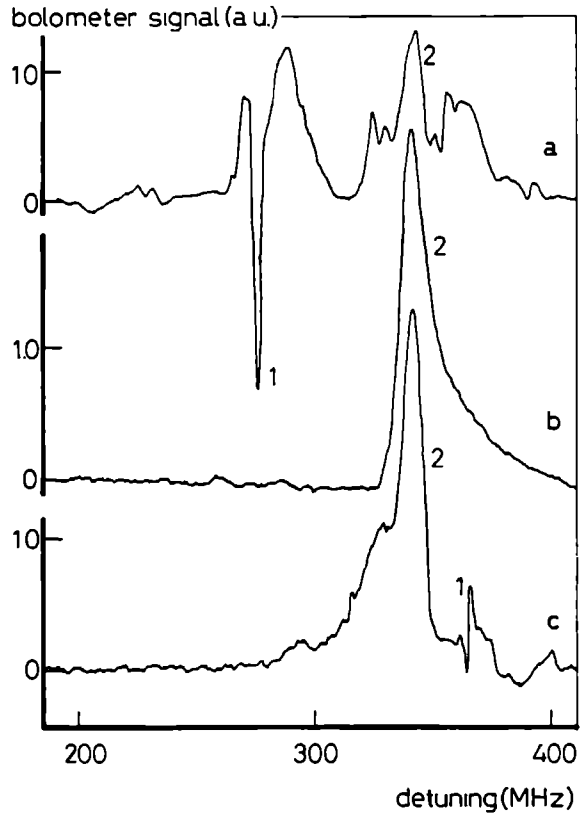


*Figure 2: The spectral region shifted 300 MHz from the 10P16 $CO_2$ laser line center for the two colour, two photon transitions, taken with three different configurations of the AOM's. In the upper spectrum, the pump laser is shifted by 100 MHz and the probe laser is shifted by 200 MHz with respect to the 10P16 $CO_2$ laser line. The spectrum in the middle is taken with the pump laser shifted by 300 MHz, no AOM is aligned in the probe laser. In the lower spectrum, the pump laser is shifted by 200 MHz and the probe laser by 100 MHz. For two colour, two photon transitions these spectra should be the same, indeed, the strong P(4) E(0) transition (peak 2) reproduces in all three spectra. Structure 1 is in resonance with the P(4) E(0) transition frequency of the probe laser. This structure and the less narrow structure around transition 2 in the upper spectrum are due to the dynamic Stark effects (section 5).*

the frequency of the $CO_2$ lasers 100 MHz up or down for a single passage of the laser beam through the AOM crystal Providing a second pass through the modulator results in another 100 MHz shift, in this way it is possible to shift the frequency of the $CO_2$ laser 200 MHz As an example the frequency region with a total shift for two colour, two photon transitions from 200 MHz to 400 MHz with respect to the 10P16 $CO_2$ laser line is presented in fig 2 In the upper spectrum, the scanned probe laser is shifted 200 MHz, while the chopped pump laser is shifted 100 MHz In the spectrum in the middle, no AOM is inserted into the probe laserbeam, both AOM's are aligned in the pump laserbeam (one double and the other single pass), resulting in a total shift of 300 MHz In the lower spectrum the role of the two lasers is interchanged with respect to the upper spectrum (i e the probe laser is shifted 100 MHz, while the pump laser is shifted 200 MHz)

Two spectral features reproduce very clearly in these spectra The feature numbered 1, is in resonance with the P(4) E(0) two photon transition utilizing two photons of the probe laser, it appears in the spectra due to the dynamical Stark effect (see section 5) Because the frequency of this transition is well known, it can be used for absolute frequency calibration The transition 2 is the same transition, but now produced utilizing one photon from each laser This are the transitions we are interested in The less narrow features in the upper spectrum around transition 2, caused by the dynamic Stark shift on the P(4) one photon quadruplet (as will be discussed in section 4), makes it difficult to assign transitions in this frequency region On the contrary, in the middle spectrum nothing is left of the less narrow structures, only a tail on transition 2 is observed due to saturation of the transition (section 4) Now it is possible to enlarge the sensitivity of the lock-in detector without overload in the regions near the P(4) two photon transition and resolve other interesting transitions which are less intense

## 5.3 Multiphoton depletion measurements

To investigate which energy levels participate mainly in the unstructured background-like multiphoton process, an Apollo laser set on top of the multiphoton signal (i e the 10P24 $CO_2$ laser line) is crossed with the molecular beam Seventy mm downstream the molecules are probed by a chopped waveguide laser set on the 10P16 $CO_2$ laser line and shifted 100 MHz by a single pass through an AOM First the spectrum without the Apollo laser is taken in fig $3^a$ with a background pressure of 300 Torr behind the nozzle and the nozzle at 300 K Some of the two photon transitions possessing J-values from 4 to 27 are indicated No changes in the intensities of the assigned two photon transitions are observed in the spectrum when the Apollo laser is turned on

Heating up the nozzle to 400 K changes the spectrum dramatically (fig $3^b$) The transitions starting from low rotational energy levels are decreased as compared with the transitions starting from higher J-values Interesting are the two transitions marked A and

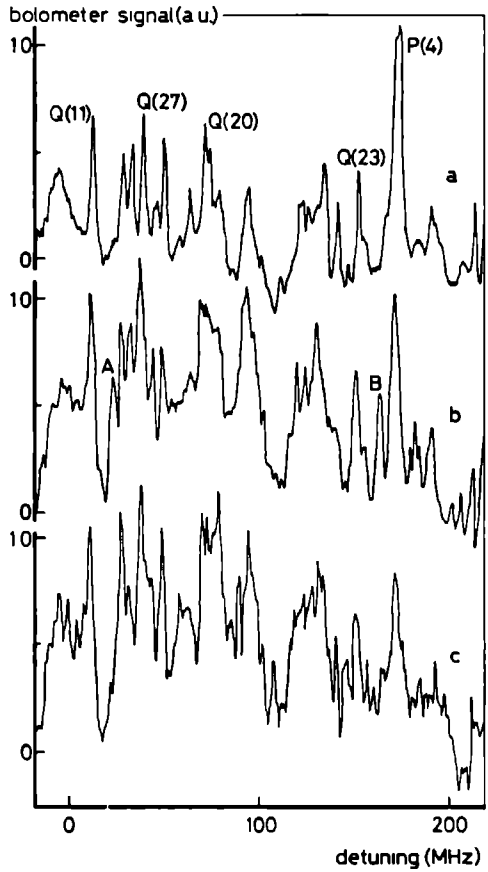


*Figure 3 Pump-probe experiments with the Apollo laser (150 W) set on the 10P24 $CO_2$ laser line, i e on top of the multiphoton signal Seventy mm downstream the interaction with the Apollo laser, the molecules are probed by a waveguide laser tuned to the 10P16 $CO_2$ laser line, its frequency is shifted 100 MHz utilizing an AOM In fig 3$^a$ the nozzle is at room temperature and the Apollo laser is turned off Some of the assigned two photon transitions are indicated in the spectra In fig 3$^b$ the nozzle is heated up to 400 K, still the Apollo laser is off As expected, the relative intensities of the transitions in the spectra change very much Special attention is required for the two transitions marked A and B, they are not observed in fig 3$^a$ From this we conclude that they are hot band transitions In fig 3$^c$ the Apollo laser is turned on, now the two hot band transitions are gone, whereas the relative intensity of the assigned two photon transitions is not changed*

B in fig.3[b], they are on frequencies where no $2\nu_3 \leftarrow 0$ transition is expected and therefore they are assigned to hot band transitions. Opening the Apollo laser, almost the same spectrum (fig.3[c]) is observed again, the relative intensities of the two photon transitions staying the same. However, the two hot band transitions vanish almost completely. From these measurements we conclude that for the multiphoton process, transitions starting from hot bands play an important role, while molecules in the ground state barely participate in the multiphoton process. This is in agreement with [6]. However, they are in contrast with measurements of V.M. Akulin et al [16], from which we expected depletions up to 30%. The measurements of [16] are critically discussed, theoretically [17]. Increasing the temperature of the nozzle again with 100 K up to 500 K, results in a broadband almost structureless spectrum. The hot band transitions come up very strongly and the spectrum becomes so dense that it is impossible to assign the $\nu_3$ transitions anymore. Putting on the Apollo laser will decreases the signal but still no spectral features are resolved.

## 5.4 Absence of power broadening and background signals

In order to investigate power broadening effects of the transitions produced by the simultaneous interaction of two lasers with a molecule, a 150 W Apollo laser, set on the 10P16 $CO_2$ laser line center is used as a pump laser. The probe laser (6 W) is scanned around the 10P16 $CO_2$ laser line, the resulting spectrum is presented in fig.4. The assigned TPTC transitions are indicated in the spectrum. In conventional spectroscopy line widths exceeding 100 MHz are expected for the intensities utilized in our experiments. However, no significant power broadening is observed; the FWHM of the measured transitions is approximately 4 MHz. This is twice as much as the FWHM of the transitions measured with only one laser (TPOC) where both participating photons change frequency.

The absence of power broadening is due to the fact that we utilize curved wave fronts; in order to increase the fluence of our lasers to investigate the transitions with low intensity factors, the lasers are tightly focused on the molecular beam (minimum waist 0.1 mm). The curved wave fronts (together with the smooth Gaussian line profiles of our lasers) are responsible for the fact that we do not observe Rabi-type transitions but RAP-transitions, for which no power broadening is expected to take place [18, 19, 20, 21].

The 20 MHz broad dip in the center of the spectrum of fig.4, is caused by a depletion of initial levels by the pump laser. The pump laser produces a background-like signal; if the probe laser frequency coincides with the frequency of the pump laser, part of the molecules are not anymore available to become excited by the probe laser; accordingly, the pump laser produces less signal resulting in negative bolometer signal. This broad dip is not very dependent on the intensities of the lasers. It appears also in all spectra with two waveguide lasers on positions where the pump and probe laser frequencies are the same. An example of such a dip is shown in fig.6, where both waveguide lasers were shifted by -200 MHz.

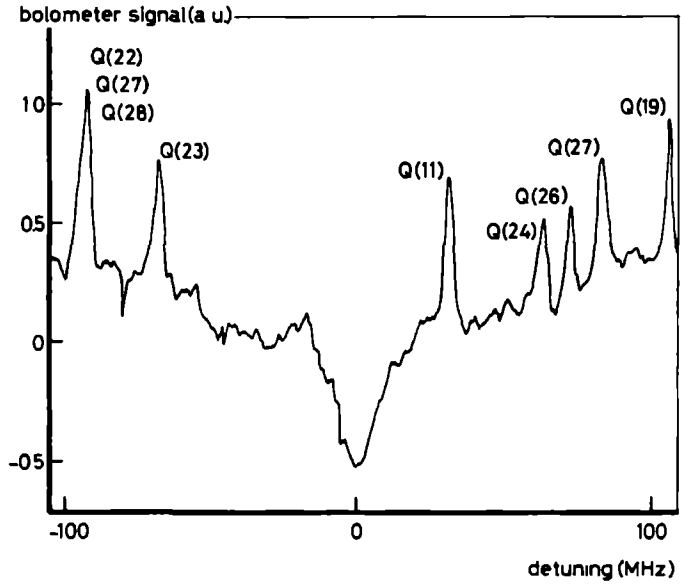


*Figure 4 Two colour, two laser transitions measured with an Apollo laser tuned to the 10P16 $CO_2$ laser line (150 W) as a pump, and a waveguide laser also set on the 10P16 $CO_2$ laser line (6 W), as a probe laser A broad dip appears in the spectra in the region where the frequencies of the pump and the probe laser are the same The widths of the assigned two photon transitions is approximately 4 MHz*

## 5.5 Dynamic Stark effects

These effects are due to the working of the chopped strong pump laser and give rise to spectral features when the probe laser is scanned, the spectral features are observed at unshifted positions (for one- and two photon transitions) but were expected to remain undetected because the probe laser is not chopped

The sharp dips in the spectra (e g structure 1 in fig 2 and fig 5) are caused by the dynamic Stark effect The pump laser couples the excited energy states of transitions - in resonance with the frequency of the probe laser - with energy levels in the quasi continuum

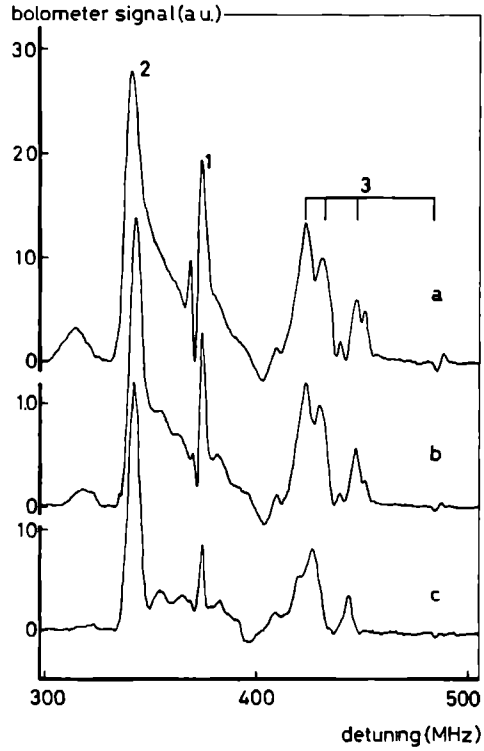


*Figure 5: Power dependence of the tail on the strong P(4) E(0) two colour, two photon transition and the Stark effects. Both the pump and the probe laser are shifted 200 MHz from the 10P16 $CO_2$ laser line. In spectrum a the intensity of the probe laser is 1 W; the pump laser is 6 W. In b the intensity of the pump laser is decreased till 3 W, in c the intensity of the pump laser is 1.5 W. The spectral feature marked 1 is due to the Stark effect of the P(4) E(0) transition in resonance with the probe laser only. The resonance of the probe laser with the P(4) one photon transitions, also causes structures to appear in the spectra. The frequencies of the P(4) quadruplet are marked under 3. Peak 2 is the P(4) E(0) two colour, two photon transition.*

This may push the two photon transition slightly out of resonance resulting in negative bolometer signal. However, at a nearby frequency this two photon transition comes into

resonance again with the photons from the probe laser, resulting in positive bolometer signal This effect is observed only for the strong two photon transitions, especially for the P(4) transitions on the 10P16 $CO_2$ laser line [6] The levels participating in two photon transitions interact with energy levels in the quasicontinuum through the pump laser, over a wide range of pump laser frequencies This is observed in the spectra, even if the pump laser is shifted several $CO_2$ laser lines the structures remain at the same probe laser frequency The shape of the structure changes depending on the intensity of the pump laser

Two other more obvious interactions of the pump laser with the final level of the transitions induced by the probe laser can give rise to signals First, the pump laser can deplete the level which is populated by the probe laser, by de-exciting the molecules However, the pump laser is fixed in frequency and the density of states in the ground state or the first excited state of the cooled molecules is not high The pump laser has to be exactly in resonance with a transition from the excited state, what will rarely happen Second, the pump laser can excite the molecule further up, either with one or two photons to a discrete level or to the quasicontinuum resulting in positive bolometer signal This second effect is much more likely to happen because the density of states increases going up on the energy ladder, in the quasi continuum there is always a transition in resonance with the laser frequency

It is difficult to distinguish in general between the dynamic Stark effects and the two possibilities discussed in the last paragraph However, in all spectra the dip is accompagnied by a positive peak, ruling out the de-excitation scheme The de-excitation scheme leads to a dip which is not accompanied by a nearby peak In all spectra this extra peak has been clearly observed, as one expects from dynamic Stark effects, thus, this mechanism is clearly present

The excitation scheme is also rather unprobable, the absence of peaks at the center frequency of transitions forms a contra-indication

A strong argument in favour of the dynamic Stark effects mechanism and the de-excitation depletion mechanism derives from the observation that the observed less narrow features do not strongly depend on the value of the pump laser frequency

In fig 5, the less narrow structure 3 is certainly due to the dynamical Stark effect In this case not the final level of a two photon transition, but the final levels of the P(4) one photon transitions [5] are affected The frequencies of the transitions of the P(4) quadruplet are marked under 3 in fig 5 The same effect is responsible for the less narrow structure around the P(4) TPTC transition (peak 2 in the upper part of fig 2) The pump laser has been shifted by 200 MHz and these features did not disappear With the pump laser working on the 10P14 or 10P18 laser transitions, the less narrow feature 3 was not observed The two photon structure 2, however, remained This probably is connected to the fact that the $2h\nu_3$ level at about 2000 $cm^{-1}$ can be coupled to the quasicontinuum by the pump laser at a greater variety of frequencies, as consequence of the increased density of states

The TPTC P(4) transition on the 10P16 $CO_2$ laser line (peak 2 in fig 2 and fig 5)

possesses a very low detuning of the intermediate level with respect to the laser frequency The intensities utilized in our experiments are more than two orders of magnitude higher than the intensities needed to saturate this transition [5] This causes saturation effects to become visible, often a tail on one side of the transition is observed Decreasing the fluence of the pump laser causes the tail to disappear much faster than the two photon transition itself This can be seen in fig 5, in which the intensity of the pump laser is decreased each time by a factor two, going from 6 W in the upper spectrum, to 3 W in the middle spectrum, to 1 5 W in the lower spectrum From these spectra it is clear that also the spectral features caused by the Stark effect on levels in resonance with the frequency of the probe laser, disappear much faster than the main signal from the TP1C transition itself

## 5.6 Two colour, two photon transitions

With the two waveguide lasers interacting simultaneously with the beam molecules new two photon transitions have been measured These transitions are included in the fitting procedure, the resulting constants for the Hamiltonian were already listed in table 2 of [6] The predicted transitions together with the measured frequencies are listed in table 1 In this table in column 2, the transitions with their ro-vibrational symmetry are listed Column shows the vibrational symmetry for transitions for which coupling to other vibrational symmetries does not disturb the energy levels too much this is only the case for transitions starting from low J-values The calculated frequencies ($\nu_S$ and $\nu_P$) and strength factors ($S_S$ and $S_P$), predicted utilizing two different representations of the terms in the Hamiltonian, are listed in columns 4 till 7 In the last column the experimental frequency of the transition is listed

The discrepancy in the two predicted frequencies $\nu_S$ and $\nu_P$ is mainly caused by the fact that the set of measured transitions, utilized in the fitting procedure is not identical in both calculations Besides the measurements described here and in [22], also two photon transitions as measured by Herlemont et al [3, 4], and one photon transitions as measured by Borde et al [23] are included in the calculations of Pierre

The two strength factors $S_S$ and $S_P$ differ by about 2 orders of magnitude due to the use of different conventions, in comparing the different transitions one should consider only the relative strengths In order not to make the listing of two photon transitions too long, transitions with a strength factor smaller than 0 1 for $S_S$ and 10 for $S_P$ are excluded These transitions are not expected to be observable in the spectra

In the last column the experimental frequencies are listed, however, if the assignment is uncertain (i e either there are no measured structures or to many measured structures around the predicted frequency) a $\star$ is listed Transitions included in the fitting procedure resulting in $\nu_S$ are marked with $\bullet$

Transitions possessing $F_{2g}$ vibrational symmetry are in good agreement with the theo-

retically predicted frequencies. Especially for the 10P14-10P18 laser line combination, the transitions are predicted very accurately due to the fact that this frequency region partially overlaps with the frequency region covered by the one laser experiments (i.e. the 10P16 region). Especially for $E_g$ vibrational symmetry, the measurements utilizing two lasers are of great importance; many new transitions are found with this symmetry. Though the predictions of the frequencies of transitions possessing this vibrational symmetry are already one order of magnitude better than the first estimates (based upon TPOC results), still work has to be done to improve the fit for the $E_g$ vibrational symmetry . Transitions possessing pure $A_{1g}$ vibrational symmetry are not predicted in the spectral regions of our measurements. For these transitions other measurements have to be performed. Utilizing $N_2O$ or isotope lasers in combination with the TPTC technique, it seems possible to improve the 67 parameters necessary to describe the $2\nu_3$ transitions in $SF_6$.

## 5.7 Three and four photon transitions

Overtone measurements on the $3\nu_3$ transitions in $SF_6$ were performed previously, [7, 8]. From these measurements we know that it is possible to measure resolved discrete three photon transitions in $SF_6$. With our experimental set-up it is possible to determine frequencies with much higher accuracy (2 MHz instead of 30 MHz). Due to selection rules it is possible to measure many more multiphoton transitions leading to levels near to the $3\nu_3$ overtone levels. For overtone transitions to the third energy level, $\Delta J$ = -1, 0 or 1 and the vibrational symmetry is restricted to $F_{1u}$, while for a three photon transition $\Delta J$ can be -3, -2, -1, 0, 1, 2, or 3 and the vibrational energy of the final level can be either $A_{2u}$, $F_{1u}$ or $F_{2u}$.

For three and four photon transitions, only preliminary results are presented. Because of the fact that the two photon transitions are not yet fitted completely, the predicted three and four photon transition frequencies $\nu_S$ and $\nu_P$ are separated often by more than 100 MHz. This makes it sometimes difficult to assign the transitions uniquely. Therefore, we approach this problem from the experimental side, in a first attempt.

To illustrate the method, the spectrum a) with both pump and probe laser shifted -200 MHz with respect to the 10P16 $CO_2$ laser line (fig.6$^a$), and the spectrum b) with the probe laser shifted -200 MHz and the pump laser shifted -100 MHz, both with respect to the 10P16 $CO_2$ laser line (fig.6$^b$) are compared. For TPTC transitions the right part of fig.6$^a$ and the left part of fig.6$^b$ are equivalent, and indeed the predicted two photon transitions in this region can be observed in both spectra. In the lower spectrum, a transition is observed between the Q(21) and the P(4) two photon transitions. This transition is not present in spectrum 6$^b$, indicating that one deals with a n photon transition with n$\geq$3. If it is a three photon transition, from spectrum 6$^a$ two possible frequency shifts can be predicted for spectrum 6$^b$. If the transition is produced utilizing two photons from the pump and one photon from the probe laser, the frequency of the transition is at $3\nu_{10P16}$-538 MHz. Another

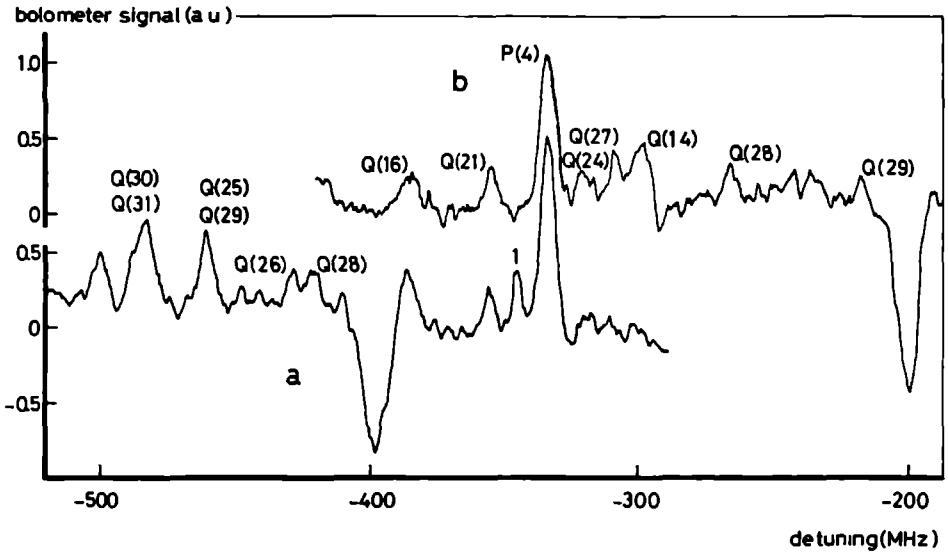


*Figure 6 In the assignment of the three photon transitions, the shift of the pump laser is very important In spectrum a and spectrum b the probe laser is scanned around the 10P16 $CO_2$ laser line and shifted -200 MHz, in spectrum a the pump laser is shifted -200 MHz with respect to the 10P16 laser line, in spectrum b this shift is only -100 MHz The assigned two photon are indicated in the spectra Transition 1 in spectrum a disappears in spectrum b, it can be assigned as a three photon transition*

possibility is that only one photon is utilized from the pump, and two photons from the probe laser, the frequency of the transition is $3\nu_{10P16}$-476 MHz Comparison of these frequencies with the calculated frequencies an assignment results for peak 1 in fig 6[a], as a R(10) $F_2(1)$ transition utilizing one photon from the pump and two photons from the probe laser

In a similar way other three and four photon transitions are assigned, they are listed in table 2 In the second column the laser line combination needed to enter the spectral region on which the transition presented in column 3 is found, is listed The predicted frequencies ($\nu_S$ and $\nu_P$) and strength factors ($S_S$ and $S_P$), calculated utilizing two different representations of the terms in the Hamiltonian and two sets of different transitions in the fitting procedure, are listed in columns 4 to 7 The experimentally determined frequencies are listed in column 8

The upper part of table 2 shows the three photon transitions. For $\nu_P$ only transitions ending on energy levels with J$\leq$10 are available at the present time, for $\nu_S$ J-values up to 30 are predicted. If in column 4 **** is listed for the strength factor, this strength factor is higher than $10^5$. Four photon transitions are only predicted in $\nu_S$; this list is limited to J-values smaller than 10. For higher J-values the time needed to calculate the four photon increases considerably because the density of states increases very fast.

The three and four photon transitions are not included in the fitting procedure; this is one reason for the discrepancies in the two theoretical predictions. In order to make the prediction of the frequencies of the three and four photon transitions more reliable it is necessary to fit first all two photon transitions and then include also step by step the three and four photon transitions, in an interactive way.

## 5.8 Outlook

Utilizing the simultaneous interaction of two lasers with $SF_6$ molecules opens a wide range of frequency regions on where many new multiphoton transitions can be measured. The one laser experiments alone do not provide enough experimental data to determine the 67 constants of the Hamiltonian which describe the $2h\nu_3$ transitions in $SF_6$ [6].

Even the use of three independent $CO_2$ lasers is planned. Herebye, the investigation of what often is termed the onset of the quasicontinuum/stochastisation becomes feasible. One expects that spectral blobs appear for certain frequencies, whereas elsewhere discrete levels will be found even for much higher energies.

Once the two photon transitions have been fit properly, the predictions of the frequencies of the three and four photon transitions will improve. Only 5 new constants have to be fit to determine the three and four photon transitions within our experimental accuracy of 2 MHz. We have still about 20 of these transitions observed which will become assignable.

## 5.9 Tables

tabel 1[a] 10P12-10P14 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | S(14) E(3) | $F_{2g}$ | 0 26 | 238 | | | * |
| 2 | S(9) E(1) | $F_{2g}$ | 0 25 | 233 | | | * |
| 3 | S(14) $A_2$(1) | $F_{2g}$ | 0 66 | 177 | | | * |
| 4 | R(11) $F_1$(2) | $F_{2g}$ | 0 10 | 302 | | | * |

Tabel 1[b] 10P12-10P16 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | R(18) $F_2$(3) | $F_{2g}$ | 0 13 | -433 | 425 | 68 | -440 |
| 2 | R(31) $F_2$(8) | | | | -367 | 308 | * |
| 3 | R(31) $F_1$(8) | | | | 367 | 308 | * |
| 4 | Q(13) $A_2$(1) | $F_{2g}$ | 3 60 | 393 | -366 | 177 | * |
| 5 | R(10) $F_1$(1) | $F_{2g}$ | 0 73 | 353 | -337 | 38 | * |
| 6 | R(10) $F_1$(2) | $F_{2g}$ | 0 53 | 353 | -337 | 29 | * |
| 7 | Q(32) E(6) | | | | 227 | 93 | * |
| 8 | R(9) $F_1$(2) | $F_{2g}$ | 1 66 | 233 | -216 | 58 | |
| 9 | R(9) $F_1$(1) | $F_{2g}$ | 5 76 | 233 | -215 | 221 | -234 |
| 10 | Q(32) $F_2$(7) | | | | 215 | 69 | * |
| 11 | Q(37) E(4) | | 0 17 | -216 | | | * |
| 12 | Q(32) $A_2$(2) | | | | -189 | 116 | * |
| 13 | Q(32) $A_2$(1) | | 0 10 | -183 | | | * |
| 14 | R(26) $F_1$(6) | | 0 14 | 2 | -24 | 332 | 27 |
| 15 | R(26) $F_2$(6) | | 0 14 | 3 | 19 | 332 | |
| 16 | R(20) $F_2$(3) | $F_{2g}$ | 0 22 | 208 | 213 | 170 | 209 |
| 17 | R(20) $F_2$(1) | $F_{2g}$ | | | 215 | 29 | * |
| 18 | Q(34) $F_2$(7) | | | | 225 | 97 | * |
| 19 | Q(30) $F_2$(7) | | | | 270 | 44 | * |
| 20 | Q(30) $F_1$(7) | | | | 276 | 44 | * |
| 21 | Q(34) $F_1$(6) | | | | 301 | 97 | * |
| 22 | R(18) E(1) | $F_{2g}$ | 0 26 | 414 | 421 | 53 | * |
| 23 | R(18) E(2) | $F_{2g}$ | 0 11 | 414 | 420 | 23 | * |

Tabel 1[c] 10P12-10P18 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu exp$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | Q(15) E(1) | $F_{2g}$ | 2 97 | 146 | | | 134 |

Tabel 1[d] 10P12-10P20 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | Q(10) $F_2$(1) | $F_{2g}$ | 0 18 | -143 | | | * |
| 2 | Q(10) $F_1$(2) | $F_{2g}$ | 0 12 | 36 | | | * |
| 3 | S(17) $A_2$(1) | $E_g$ | 0 12 | 146 | | | * |

Tabel 1[e] 10P12 10P22 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | R(12) E(2) | $E_g$ | 0 12 | -16 | | | * |
| 2 | S(6) $F_2$(1) | $E_g$ | 10 06 | 4 | | | * |
| 3 | S(6) $F_1$(1) | $E_g$ | 10 06 | 479 | | | * |

Tabel 1f. 10P14-10P16 laser line combination

| nr | transition | vib sym. | $S_S$ a u. | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u. | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | Q(11) $F_1(2)$ | $F_{2g}$ | 1.39 | -484 | -470 | 26 | -481 |
| 2 | Q(11) $F_1(1)$ | $F_{2g}$ | 0 12 | -484 | -470 | 38 | |
| 3 | R(9) $F_1(3)$ | $F_{2g}$ | 30 02 | -369 | -368 | 1729 | -373 |
| 4 | S(33) E(3) | | 1 83 | -128 | -127 | 2798 | -126 |
| 5 | S(33) $F_1(5)$ | | 0.57 | -71 | -69 | 2092 | -69 |
| 6 | Q(17) $F_2(2)$ | $F_{2g}$ | | | -37 | 98 | |
| 7• | Q(17) $F_2(3)$ | $F_{2g}$ | 0.19 | -48 | -37 | 152 | -47 |
| 8 | S(33) $A_1(2)$ | | | | 66 | 692 | * |
| 9 | S(36) $F_2(8)$ | | 0 24 | 28 | 89 | 916 | * |
| 10 | S(36) E(5) | | 0.76 | 28 | 89 | 1220 | * |
| 11 | S(36) $A_2(3)$ | | 1 86 | 29 | 89 | 1526 | * |
| 12 | S(32) $F_2(3)$ | | 0 73 | 64 | 157 | 2786 | * |
| 13• | Q(21) $F_2(1)$ | $F_{2g}$ | 0.19 | 76 | 86 | 371 | 76 |
| 14• | R(7) E(1) | $F_{2g}$ | 1212 79 | 127 | 130 | 11071 | 132 |
| 15 | Q(4) $F_2(1)$ | $F_{2g}$ | 118.94 | 140 | | | 141 |
| 16 | Q(16) $F_2(4)$ | $F_{2g}$ | 0.12 | 307 | 319 | 112 | 317 |
| 17 | Q(16) $F_2(2)$ | $F_{2g}$ | | | 320 | 59 | |
| 18 | S(32) $F_1(3)$ | | 0.76 | 359 | 351 | 2751 | * |
| 19 | S(34) E(4) | | 1 29 | 404 | 418 | 2099 | * |
| 20 | S(34) $F_2(6)$ | | .40 | 413 | 427 | 1673 | * |
| 21 | S(35) E(5) | | .94 | 413 | 448 | 1706 | * |
| 22 | S(35) $F_1(7)$ | | .31 | 414 | 449 | 1280 | * |
| 23 | S(34) $A_2(2)$ | | 3.10 | 430 | 445 | 2620 | * |
| 24 | Q(4) $F_1(1)$ | $F_{2g}$ | $7\ 10^5$ | 435 | 443 | $5\ 10^5$ | 429 |
| 25 | S(36) $A_1(2)$ | | | | 451 | 427 | * |

Tabel 1g: 10P14-10P18 laser line combination

| nr | transition | vib sym. | $S_S$ a.u. | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a.u. | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | S(17) $F_1(2)$ | $E_g$ | 0 63 | -473 | | | * |
| 2 | Q(34) $F_1(1)$ | | 2.40 | -419 | -423 | 12980 | * |
| 3 | Q(34) E(1) | | 7.54 | -382 | -385 | 17336 | -382 |
| 4 | Q(34) $F_2(1)$ | | 2.40 | -346 | -349 | 13023 | -347 |
| 5 | Q(33) $A_1(1)$ | | | | -238 | 6605 | -236 |
| 6 | Q(33) $F_1(1)$ | | 5.48 | -187 | -190 | 16796 | -187 |
| 7 | R(35) $F_2(6)$ | | | | -154 | 194 | * |
| 8 | Q(13) $A_2(1)$ | $F_{2g}$ | 0 61 | -146 | | | -148 |
| 9 | Q(33) $F_2(1)$ | | 5 47 | -140 | -143 | 16776 | -143 |
| 10 | R(35) $F_1(6)$ | | | | -138 | 195 | * |
| 11 | Q(33) $A_2(3)$ | | 9.27 | -95 | | | |
| 12 | Q(33) $A_2(2)$ | | 1988.28 | -95 | -97 | 28141 | -96 |
| 13 | Q(33) $A_2(1)$ | | 199 75 | -95 | | | |
| 14 | S(18) $F_1(3)$ | $E_g$ | 0.61 | -39 | | | -59 |
| 15 | Q(32) $F_1(1)$ | | 0.97 | -37 | -40 | 1426 | -40 |
| 16 | R(31) $F_2(6)$ | | 1.16 | -8 | -13 | 3286 | * |
| 17 | R(31) $F_1(7)$ | | 1.16 | -3 | -8 | 3287 | * |
| 18 | Q(24) $A_2(1)$ | | 0.92 | -1 | -2 | 345 | -3 |
| 19 | Q(24) $A_2(2)$ | | 0.17 | 2 | | | |
| 20 | Q(32) E(1) | | 3.11 | 24 | 21 | 1902 | 24 |
| 21 | S(18) E(2) | $E_g$ | 2 00 | 37 | | | 16 |
| 22 | Q(32) $F_2(1)$ | | 1 03 | 82 | 80 | 1427 | 83 |
| 23 | Q(22) $F_1(1)$ | $F_{2g}$ | | | 91 | 64 | 92 |
| 24 | Q(31) $F_2(4)$ | | 0.23 | 103 | | | |
| 25 | Q(31) $F_2(1)$ | | 0.71 | 103 | 100 | 663 | 102 |
| 26 | Q(31) $F_2(2)$ | | 0.21 | 103 | | | |
| 27 | Q(31) $F_2(6)$ | | 0.26 | 103 | | | |
| 28 | Q(23) $F_2(1)$ | $F_{2g}$ | | | 140 | 109 | 139 |
| 29 | Q(30) $A_2(1)$ | | 6.53 | 158 | 155 | 2080 | 156 |
| 30 | Q(30) $A_2(2)$ | | 1.07 | 158 | | | |
| 31 | Q(31) E(4) | | 0.80 | 179 | | | |
| 32 | Q(31) E(1) | | 2 10 | 179 | 177 | 885 | 178 |
| 33 | Q(31) E(2) | | 0 63 | 179 | | | |

Tabel 1[g] continued

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 34 | Q(31) E(3) | | 0 70 | 179 | | | |
| 35 | Q(27) $A_1$(1) | | | | 223 | 2512 | 222 |
| 36 | Q(31) $F_1$(1) | | 0 71 | 256 | 253 | 665 | 253 |
| 37 | Q(31) $F_1$(3) | | 0 20 | 256 | | | |
| 38 | Q(31) $F_1$(4) | | 0 23 | 256 | | | |
| 39 | Q(31) $F_1$(5) | | 0 26 | 256 | | | |
| 40 | Q(30) $F_2$(1) | | 0 83 | 258 | 256 | 1249 | 257 |
| 41 | Q(30) $F_2$(2) | | 0 11 | 258 | | | |
| 42 | Q(30) $F_2$(3) | | 0 12 | 258 | | | |
| 43 | Q(30) $F_2$(5) | | 0 14 | 258 | | | * |
| 44 | Q(29) $F_2$(1) | | 1 86 | 279 | 278 | 3521 | 278 |
| 45 | Q(25) $F_2$(1) | | 0 24 | 280 | 281 | 444 | 283 |
| 46 | Q(26) $F_1$(1) | | 0 62 | 312 | 313 | 1259 | 312 |
| 47 | Q(28) $F_1$(1) | | 36 93 | 320 | 320 | 78101 | 320 |
| 48 | Q(30) $F_1$(3) | | 0 10 | 355 | | | |
| 49 | Q(30) $F_1$(1) | | 0 83 | 355 | 353 | 1251 | 356 |
| 50 | Q(30) $F_1$(6) | | 0 14 | 355 | | | |
| 51 | Q(30) $F_1$(5) | | 0 12 | 355 | | | |
| 52 | Q(29) E(1) | | 6 08 | 407 | 406 | 4698 | 407 |
| 53 | Q(29) E(2) | | 0 20 | 407 | | | |
| 54 | Q(29) E(3) | | 0 61 | 407 | | | |
| 55 | Q(29) E(4) | | 0 31 | 407 | | | |
| 56 | Q(24) $F_2$(1) | | 0 12 | 425 | 424 | 209 | 426 |
| 57 | Q(27) $F_1$(1) | | 3 61 | 435 | 434 | 7592 | 436 |
| 58 | Q(30) $A_1$(1) | | | | 446 | 417 | 447 |
| 59 | R(25) $F_2$(6) | | 0 31 | 466 | 464 | 617 | 464 |
| 60 | R(25) $F_1$(7) | | 0 31 | 467 | 465 | 617 | |
| 61 | S(20) $F_1$(5) | $E_g$ | 0 65 | 474 | | | |
| 62 | S(20) E(4) | $E_g$ | 2 01 | 474 | | | 473 |
| 63 | Q(28) E(1) | | 116 75 | 475 | 476 | 103519 | 476 |
| 64 | Q(28) E(2) | | 0 13 | 479 | | | |
| 65 | Q(28) E(3) | | 0 15 | 479 | | | |

Tabel 1[h] 10P14 10P20 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | R(14) $F_2$(3) | $E_g$ | 0 54 | 9 | | | 1 |
| 2 | P(10) $F_1$(1) | $F_{2g}$ | 0 16 | 140 | | | 164 |
| 3 | R(17) E(2) | $E_g$ | 1 55 | 352 | | | 360 |
| 4 | P(24) $A_2$(1) | | 0 10 | 430 | | | * |
| 5 | R(16) $A_2$(1) | $E_g$ | 4 08 | 447 | | | 445 |
| 6 | Q(31) $F_1$(7) | | 0 28 | 496 | 436 | 1235 | * |
| 7 | Q(31) $F_2$(6) | | 0 28 | 497 | 436 | 1235 | * |

Tabel 1[i] 10P14 10P22 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | R(26) E(2) | | 0 12 | 170 | -187 | 99 | * |
| 2 | R(21) $A_2$(2) | $E_g$ | 0 12 | 102 | | | * |
| 3 | R(22) $A_2$(1) | $E_g$ | | | 125 | 15 | * |
| 4 | R(22) E(2) | $E_g$ | | | 476 | 16 | * |

Tabel 1[j] 10P14-10P24 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | P(7) $F_1$(2) | $E_g$ | 8 99 | -319 | | | * |
| 2 | P(7) E(1) | $E_g$ | 52 50 | 468 | | | * |

Tabel 1[k] 10P16-10P18 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | R(22) E(1) | $E_g$ | 8 84 | -453 | 493 | 2485 | -450 |
| 2 | R(22) $F_1$(1) | $E_g$ | 2 84 | -375 | -415 | 1884 | -374 |
| 3 | R(22) $F_1$(3) | $E_g$ | 2 50 | -375 | | | |
| 4 | P(11) $F_2$(3) | $F_{2g}$ | 0 18 | -374 | | | |
| 5 | R(17) $F_2$(2) | $E_g$ | 5 94 | -353 | 251 | 1362 | -349 |
| 6 | R(17) $F_2$(3) | $E_g$ | 0 13 | -353 | -351 | 31 | |
| 7 | R(26) $F_2$(1) | | | | -276 | 71 | |
| 8 | R(26) E(1) | | | | -274 | 91 | -274 |
| 9 | R(26) $F_1$(1) | | | | 273 | 54 | |
| 10 | R(26) $F_1$(1) | | | | -256 | 61 | -255 |
| 11 | R(26) E(1) | | 0 15 | -240 | -243 | 57 | -242 |
| 12 | P(20) $F_1$(3) | $F_{2g}$ | 2 01 | -208 | -206 | 499 | -201 |
| 13 | R(26) $F_2$(1) | | | | -178 | 73 | 163 |
| 14 | R(26) E(1) | | 0 12 | -144 | -161 | 66 | -147 |
| 15 | Q(36) $F_2$(7) | | | | -137 | 1148 | 136 |
| 16 | Q(36) $F_1$(7) | | | | -136 | 1148 | |
| 17 | P(29) $A_1$(2) | | | | -48 | 341 | |
| 18• | R(18) $F_2$(2) | $E_g$ | 5 12 | -46 | 48 | 1549 | -41 |
| 19 | Q(36) $F_1$(8) | | 34 | -45 | | | |
| 20 | P(29) $F_1$(7) | | 1 23 | -44 | -47 | 1024 | |
| 21• | P(29) E(5) | | 4 01 | 44 | -46 | 1366 | -45 |
| 22 | Q(36) $F_2$(7) | | 0 14 | -43 | | | |
| 23 | Q(36) $F_2$(8) | | 0 34 | -43 | | | |
| 24 | Q(36) $F_1$(7) | | 0 14 | -42 | | | |
| 25 | R(26) $A_2$(1) | | 0 14 | -8 | -21 | 38 | -6 |
| 26• | O(7) $F_1$(2) | $F_{2g}$ | 835 44 | 4 | 0 | 5564 | 6 |
| 27 | O(7) $F_1$(1) | $F_{2g}$ | 99 73 | 4 | 0 | 702 | |
| 28 | R(13) $F_2$(3) | $E_g$ | 7 87 | 142 | 164 | 654 | 161 |
| 29 | O(9) $F_1$(2) | $F_{2g}$ | 5 36 | 152 | 152 | 133 | |
| 30 | O(9) $F_1$(3) | $F_{2g}$ | 0 36 | 152 | | | |
| 31• | O(9) $F_1$(1) | $F_{2g}$ | 22 33 | 152 | 152 | 34 | 155 |
| 32 | P(18) $F_2$(2) | $F_{2g}$ | 2 45 | 285 | 291 | 430 | 287 |
| 33 | R(13) $F_1$(4) | $E_g$ | 7 87 | 320 | 342 | 653 | 354 |
| 34 | R(18) E(1) | $E_g$ | 16 21 | 479 | 477 | 2022 | 480 |

Tabel 1[l] 10P16-10P20 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | P(37) E(4) | | 3 29 | -482 | | | 483 |
| 2 | P(37) E(3) | | 2 89 | -479 | | | |
| 3 | P(17) E(2) | $F_{2g}$ | 0 34 | -460 | -471 | 25 | -468 |
| 4 | P(18) E(1) | $F_{2g}$ | 0 43 | -446 | -456 | 46 | -455 |
| 5 | O(16) $F_2$(2) | $F_{2g}$ | 0 12 | -419 | | | |
| 6 | P(17) $F_2$(1) | $F_{2g}$ | 0 22 | -331 | -342 | 21 | -345 |
| 7 | O(16) $F_1$(1) | $F_{2g}$ | 0 12 | -312 | | | |
| 8 | O(16) $F_1$(4) | $F_{2g}$ | 0 11 | -308 | | | |
| 9 | O(16) $F_1$(2) | $F_{2g}$ | 0 15 | -308 | | | |
| 10 | P(35) $F_2$(3) | | 1 09 | -250 | -326 | 4646 | * |
| 11 | R(20) $F_1$(3) | $E_g$ | | | -171 | 32 | -174 |
| 12 | O(23) $A_2$(2) | $F_{2g}$ | 0 11 | -96 | | | |
| 13 | O(23) E(1) | $F_{2g}$ | 0 15 | -95 | | | -89 |
| 14 | R(20) $F_2$(3) | $E_g$ | | | -66 | 39 | -64 |
| 15 | P(17) $A_2$(1) | $F_{2g}$ | 5 60 | -44 | -56 | 52 | -47 |
| 16 | P(37) $F_2$(4) | | 0 88 | 197 | 107 | 4453 | * |
| 17 | P(39) $F_2$(4) | | 0 67 | 235 | 152 | 3913 | * |
| 18 | P(35) $F_1$(3) | | 1 03 | 265 | 199 | 4379 | * |
| 19 | R(21) $F_1$(3) | $E_g$ | | | 360 | 23 | 356 |
| 20 | O(11) $A_2$(1) | $F_{2g}$ | 4 99 | 399 | | | * |

Tabel 1[m] 10P16-10P22 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | Q(37) $F_1(9)$ | | | | -411 | 409 | * |
| 2 | Q(37) $A_1(3)$ | | | | -411 | 136 | * |
| 3 | Q(37) E(6) | | 0 24 | -409 | -411 | 645 | * |
| 4 | Q(25) $A_2(2)$ | | 2 30 | -264 | -287 | 600 | -263 |
| 5 | Q(25) $F_2(4)$ | | 0 30 | -147 | -169 | 356 | * |
| 6 | Q(25) E(3) | | 0 96 | -91 | -112 | 475 | * |
| 7 | Q(18) $F_1(2)$ | $E_g$ | 0 18 | -68 | -88 | 65 | -72 |
| 8• | P(6) $F_1(1)$ | $E_g$ | 225 92 | -5 | 26 | 708 | -4 |
| 9 | Q(22) E(2) | $E_g$ | 0 60 | -4 | -19 | 193 | |
| 10 | Q(22) E(1) | $E_g$ | | | -17 | 29 | |
| 11 | Q(18) E(1) | $E_g$ | 0 68 | 108 | 88 | 109 | 99 |
| 12 | Q(20) $A_2(1)$ | $E_g$ | 0 33 | 198 | 180 | 34 | * |
| 13 | Q(18) $F_2(2)$ | $E_g$ | 0 29 | 311 | 291 | 108 | 301 |
| 14 | P(6) $F_2(2)$ | $E_g$ | 234 39 | 327 | 358 | 742 | |
| 15 | P(6) $F_2(1)$ | $E_g$ | 408 07 | 327 | 358 | 1231 | 298 |

Tabel 1[n] 10P16-10P24 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | Q(39) $A_2(3)$ | | 0 10 | 376 | | | * |
| 2 | O(9) $F_2(2)$ | $E_g$ | 0 17 | 420 | 448 | 13 | * |
| 3 | P(39) $F_1(2)$ | | 0 70 | 430 | | | * |
| 4 | P(39) E(1) | | 1 99 | 444 | | | * |
| 5 | P(39) $F_2(2)$ | | 0 67 | 457 | | | * |

Tabel 1[o] 10P18-10P20 laser line combination

| nr | transition | vib sym | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u. | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1• | P(6) $A_2(1)$ | $E_g$ | 944 90 | -435 | | | -436 |
| 2 | Q(29) $F_1(6)$ | | | | -423 | 14 | |
| 3 | Q(29) $F_2(6)$ | | | | -421 | 14 | -420 |
| 4 | Q(29) $F_2(1)$ | | 5 51 | -403 | | | -398 |
| 5 | O(38) E(4) | | 0 27 | -81 | | | |
| 6 | O(38) E(3) | | 0 26 | -79 | -142 | 1098 | * |
| 7• | P(7) $F_1(1)$ | $E_g$ | 247 82 | -58 | | | -59 |
| 8 | O(15) $A_2(2)$ | $F_{2g}$ | 0 17 | -56 | | | |
| 9 | O(15) $A_2(1)$ | $F_{2g}$ | 0 10 | -56 | | | |
| 10 | Q(22) $A_2(1)$ | $E_g$ | 0 12 | -9 | | | -6 |
| 11 | O(38) $F_2(4)$ | | | | 15 | 829 | * |
| 12 | O(37) E(5) | | 0 43 | 100 | | | |
| 13 | O(37) E(4) | | 0 40 | 103 | 24 | 1381 | * |
| 14 | O(37) $F_1(7)$ | | 0 13 | 120 | | | |
| 15 | O(37) $F_1(6)$ | | 0 13 | 120 | 40 | 1036 | * |
| 16 | O(37) $A_1(2)$ | | | | 75 | 346 | * |
| 17 | P(29) $F_1(2)$ | | | | 407 | 11 | * |

Tabel 1[p] 10P18-10P22 laser line combination

| nr | transition | vib. sym | $S_S$ a u. | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a.u. | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | P(17) E(1) | $E_g$ | 0.23 | -365 | | | * |
| 2 | P(17) E(2) | $E_g$ | 0.29 | -365 | | | * |
| 3 | P(17) E(3) | $E_g$ | 0 17 | -365 | | | * |
| 4 | O(8) $F_1$(2) | $E_g$ | 2 06 | -181 | | | -188 |
| 5 | P(14) $F_2$(1) | $E_g$ | 0 25 | -134 | | | -138 |
| 6 | P(14) $F_2$(2) | $E_g$ | 0 45 | -134 | | | |
| 7 | Q(36) $F_2$(4) | | | | -24 | 91 | -13 |
| 8 | O(8) E(2) | $E_g$ | 6 23 | 13 | | | 10 |
| 9 | Q(37) $F_1$(5) | | | | 178 | 126 | * |

Tabel 1[q]: 10P18-10P24 laser line combination

| nr | transition | vib. sym. | $S_S$ a u. | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a.u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | O(33) $F_1$(1) | | 0 23 | 254 | | | * |
| 2 | O(33) $F_1$(2) | | 1 39 | 254 | | | * |
| 3 | O(33) $F_1$(3) | | 0.24 | 254 | | | * |
| 4 | O(33) $F_1$(4) | | 15.71 | 254 | | | * |
| 5 | O(33) $F_1$(5) | | 0 25 | 254 | | | * |

Tabel 1[r]: 10P20-10P22 laser line combination

| nr | transition | vib. sym. | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | P(37) $A_2$(1) | | 0 10 | 180 | | | * |

*Table 1: For each combination of laser lines, the predicted two colour, two photon transitions are listed in column 1, with their ro-vibrational symmetries. J-values up till 40 are included in the table; higher J-values are not observable in our spectra because of the poor population of these levels. In the third column, the vibrational symmetry is presented, this is only possible for transitions starting from low J-values because for higher J-values, the interaction between the different energy levels of the different symmetry branches causes the energy levels to shift. Due to this interaction the transitions can not be assigned to one vibrational symmetry anymore.*

*The calculated frequencies ($\nu_S$ and $\nu_P$ utilizing two different representations and different sets of lines in the fitting procedure) are listed in column 5 and 6; their strength factors are listed in column 4 and 7, respectively. In comparing the strength factors, $S_S$ is aproximately two orders of magnitude smaller than $S_P$; only the relative strength of two different transitions can be compared with another. The experimental frequencies are listed in column 8. If it is not possible to assign a transition uniquely a $\star$ is plotted in column 8. Transitions utilized in the fitting procedure are marked with $\bullet$.*

tabel 2 3 and 4 photon transitions

| nr | $CO_2$ lines | transition | $S_S$ a u | $\nu_S$ [MHz] | $\nu_P$ [MHz] | $S_P$ a u | $\nu_{exp}$ [MHz] |
|---|---|---|---|---|---|---|---|
| 1 | 2P14+P22 | R(6) $F_1(1)$ | 16 | -239 | -130 | $5\,10^4$ | -210 |
| 2 | 3P16 | R(10) $F_2(1)$ | 2 | -420 | | | -338 |
| 3 | 3P16 | N(5) E(1) | 1900 | 990 | | | 852 |
| 4 | 2P16+P20 | Q(11) $F_1(2)$ | **** | -32 | -20 | $7\,10^6$ | 2 |
| 5 | 2P16+P14 | R(16) E(2) | 22 | -24 | | | -10 |
| 6 | 2P16+P14 | S(7) $F_2(1)$ | 3 | -110 | 46 | $5\,10^3$ | -116 |
| 1 | 2P16+2P18 | Q(5) $F_1(2)$ | **** | -308 | | | -312 |
| 2 | 2P16+2P22 | N(4) $F_1(1)$ | **** | 326 | | | 278 |

*Table 2: Predicted three and four photon transitions with experimental frequencies. In column 2 the combination of laser lines (needed to enter the spectral region in which the transitions listed in column 3 can be measured) is listed. The predicted frequencies and strength factors are listed in column 4 to 7; the measured frequencies are given in column 8. If a transition has a strength factor $S_S$ ****, it is stronger than 100,000. For the four photon transitions no listing of $\nu_P$ is available at this moment. To get the calculated frequencies in better agreement with each other and with the experimental data, it is necessary to fit all two photon transitions and to include the three and four photon transitions in the fitting procedure.*

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# Outlook

Measurements utilizing two counterpropagating $CO_2$ lasers interacting simultaneously with $SF_6$ molecules provided many new data which are used to investigate multiphoton transitions in $SF_6$ (chapter 4 and 5 of this thesis and [1, 2]) Utilizing this new technique together with the one laser measurements (chapter 2 and 3 of this thesis and [3]) two photon transitions starting from energy levels possessing $F_{2g}$ vibrational symmetry are fit within 3 MHz

For the transitions ending on energy levels possessing $E_g$ vibrational symmetry, the discrepancie between theoretically predicted and experimentally determined frequencies has been diminished one order of magnitude utilizing only the $^{12}C^{16}O_2$ isotope as a laser medium These transitions are now predicted with an accuracy of $\pm$ 20 MHz Utilizing a laser tuned to the 10P14 $^{12}C^{16}O_2$ transition in combination with a laser tuned to the 10R42 $^{13}C^{16}O_2$ transition [4], the frequency region in which transitions possessing $E_g$ vibrational symmetry and low J-values can be probed, in the future this will lead probably to a further improved Hamiltonian

For the two photon transitions possessing $A_{1g}$ vibrational symmetry, a laser tuned to the 10P14 $^{12}C^{16}O_2$ transition has to be combined with a laser tuned to the 10P34 $^{12}C^{18}O_2$ transition in order to enter the frequency region in which transitions are expected Combinations of the $CO_2$ isotope lasers and the $N_2O$ laser will probably provide enough data to come to a quantitative understanding also of these $2h\nu_3$ $A_{1g}$ levels

Three lasers can be utilized in a similar way, interacting at the same time with the $SF_6$ molecules, many multiphoton transitions with energies of 3000 $cm^{-1}$ or more can be investigated in this way

Due to the interaction with dark states the energy levels of the transitions (starting from the ground state) might be shifted Comparing the theoretically predicted frequencies with the measured ones will provide information about these effects $SF_6$ is a very special molecule in which these dark state interactions appear to be practically absent for excitation energies $\leq$ 3000 $cm^{-1}$ Once the three photon transitions are fit, the four and five photon transitions can be predicted with the same set of parameters for the Hamiltonian The 5000 $cm^{-1}$ region is generally excepted to be the start of the quasicontinuum/stochastisation [5] However, probably not all the frequency regions will be affected by this process In some frequency regions spectral blobs are expected to appear due to the start of the quasicontinuum In other regions, even with much higher energies we expect still isolated transitions giving rise to sharp spectral features An interesting subject of further investigation is, up to what

energy isolated transitions can be resolved and assigned.

Utilizing the high power Apollo laser [6] with its $TEM_{00}$ mode to further excite the molecules from a well known energy level will provide interesting information on the dependence of multiphoton excitation and multiphoton dissociation on the rotational and vibrational energy of the molecules.

Concerning the field of molecular quantum electronics we want to draw the attention to three interesting items of investigation; first of all, the Stark effects can be investigated utilizing two counterpropagating lasers. If one of the lasers is set on the P(4) E(0) one photon transition shifted 250 MHz with respect to the 10P16 $CO_2$ laser line with full power (i.e. 600 times the intensity needed to saturate this transition), the energy levels involved will be shifted. The ground state level shift of this transition can be probed by the second laser, utilizing the P(4) E(0) two photon transition shifted 174 MHz from the 10P16 $CO_2$ laser line. An interesting feature in these measurements is that the intermediate level of the two photon transition is also shifted giving rise to a change of transition probability. Theoretical predictions and preliminar measurements are at hand.

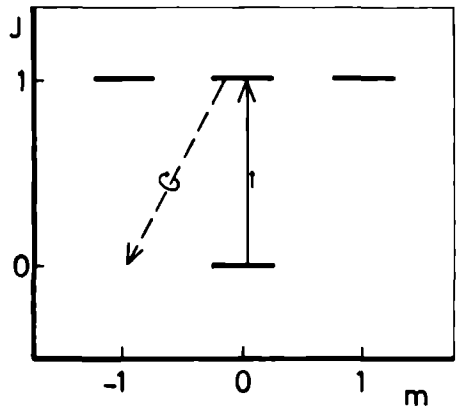


*Figure 1: Effects of polarized light on R transitions starting from the J=0 level. The molecule is excited by linearly polarized light ($\Delta m=0$). Depletion of the excited level utilizing circularly polarized light is not possible; only linearly polarized light can depopulate the excited level taking the molecule again to the ground state.*

Secondly, exploring the two photon Ramsey fringes [7] it is possible to create a new frequency standard in the infrared region. In order to do so, the molecular beam is crossed

twice by the same laser radiation which is afterwards retro-reflected In this way, the time of flight of the molecules between the two interaction regions of the standing wave laser radiation with the molecular beam determines the distance between the Ramsey fringes With this method we expect to produce a frequency standard with an accuracy much higher than 1 Hz Ultra stable lasers are evidently needed to perform these experiments

A third interesting subject of future research concerns polarization effects [8], expected to be pronounced for the transitions starting from low J-values One photon R transitions starting from J=0, pump the molecules up for 100% (under RAP conditions [9, 10]), with linearly polarized light, to the level with J=1 and m=0 Probing this level with a second laser tuned to the same frequency, produces a (negative) bolometer signal if this second deexcitation laser is linearly polarized parallel to the polarization of the excitation laser If circularly polarized light is used, no bolometer signal will be observed (fig 1) For transitions starting from J=1 levels the signal will be decreased by 33% going from linearly to circularly polarized light For transitions starting from J=2 this effect is 20%, and for transitions starting from levels with J=3 the effect will be only 11%, just at the limit of our experimental accuracy

So far, the reasoning is based on simple straightforward selection rules By applying a three step excitation to the $SF_6$ molecules, the possibility exists to produce spinning molecules with their rotation axis oriented to a high degree In fig 2, the proposed experiment shows a) an excitation from J"=4→J'=3, a two photon excitation with $\Delta m=+2$, b) a de-excitation with the same laser frequency, but with a change of circular polarization so that again $\Delta m=+2$ For the third step we have two options

$c_1$) employs an 1 $h\nu$ excitation with $\Delta m=+1$ to a J=3 level, in this way $SF_6$ molecules are produced with m=+1, +2 and +3, all other sublevels are unoccupied

$c_2$) is a $2h\nu$ transition to J=3, populated sublevels are those with m=+1 and +2

Option $c_1$) needs two different laser frequencies, option $c_2$) works with a single laser frequency Note that in all steps RAP processes are active so that the total population is transferred each time

The molecules excited to well characterised energy levels can be used in a wide range of experiments We collaborate with the group of Duren (Gottingen) to investigate the dependence of elastic, non-elastic and reactive collisions of $SF_6$ molecules with Na atoms on the internal energy of the $SF_6$ Another way to employ the highly excited $SF_6$ molecules is chosen in collaboration with the group of S Iannotta (Trento) In their machine a molecular beam can be scattered on a surface The dependence of the surface scattering on the internal energy distribution is the subject of this investigation The possibility of orienting excited $SF_6$ molecules as indicated in the previous paragraph, allows new scattering experiments (gas phase and surface collisions) Note that the oriented molecule $SF_6$ does not possess an electric dipole moment which normally is required for orientation The asymmetrically corrugated surface mainly used by the Trento group, GaSe, in combination with the oriented

spinning $SF_6$ molecules is expected to show very interesting effects, e g strong out of plane scattering

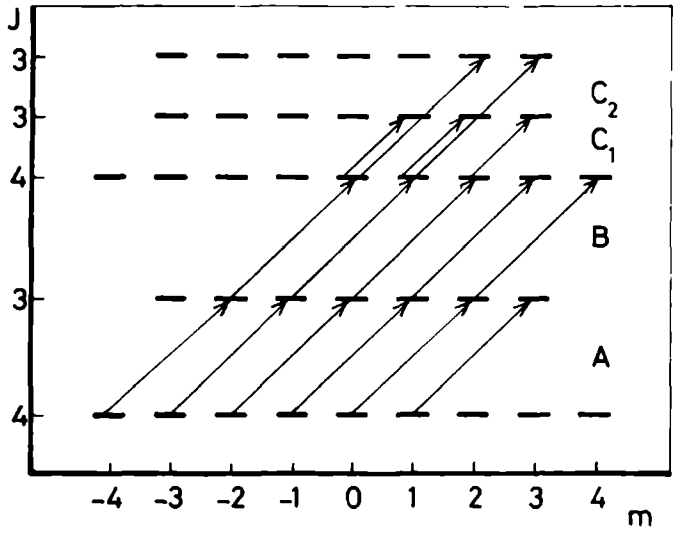


*Figure 2 Excitation scheme to produce oriented spinning $SF_6$ molecules utilizing three step excitation with circularly polarized laser radiation a) 2 hν excitation J"=4→J'=3 b) 2 hν de-excitation with J'=3→J"=4 And finally either c1) 1 hν or c2) 2 hν excitation both to a level with J=4 Note that on the vertical axis sequential changes of J are shown by arrows, it does not necessarily mean that the energy increases*

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# Samenvatting

## Hoge resolutie multilaserexperimenten aan multifotonovergangen in $SF_6$

In dit proefschrift worden metingen aan $SF_6$ moleculen die met behulp van fotonen met een golflengte van $\pm$ 10 $\mu$m in trilling worden gebracht gepresenteerd Hierbij worden de $SF_6$ moleculen eerst in een zo laag mogelijke energietoestand gebracht (de grondtoestand) door ze sterk te koelen Dit gebeurt tijdens een expansie door een zeer kleine opening (de nozzle met een diameter van 50 $\mu$m) in het vacuum van de opstelling Na deze expansie bewegen de moleculen zich allemaal met ongeveer dezelfde snelheid ($\pm$ 1200 m/s) in dezelfde richting

De totale hoeveelheid energie die de moleculen nu nog bezitten (translationele, vibrationele en rotationele) wordt gemeten met een temperatuurgevoelig weerstandje (de bolometer), waar we de moleculen op laten vallen Als we de $SF_6$ moleculen opwarmen met behulp van een $CO_2$ laser (waarmee we een specifieke trilling in het $SF_6$ aanslaan, in ons geval de $\nu_3$ mode), zal de weerstand van de bolometer veranderen Hoeveel de weerstand verandert is een maat voor de hoeveelheid energie opgenomen in het $SF_6$

$SF_6$ is een interessant molecuul het energiespectrum kan ruwweg verdeeld worden in drie stukken Het eerste stuk bestaat uit een gebied waarin we te maken hebben met discrete energieniveaus (tot $\pm$ 5000 $cm^{-1}$), geleidelijk gaat dit over in een gebied waar de energieniveaus zo dicht bij elkaar komen te liggen, dat er altijd een resonante overgang aanwezig is binnen de bandbreedte van de lasers (het quasicontinuum) Bij nog hogere energieen verbreden de niveaus vanwege optredende dissociatie, zodat men niet meer kan spreken van geisoleerde overgangen (het continuum)

In een poging te onderzoeken hoe het quasicontinuum tot stand komt, zal eerst goed onderzocht moeten worden wat er in het gebied met energieen lager dan 5000 $cm^{-1}$ precies aan de hand is Om de constanten in de Hamiltoniaan, die nodig is om de $\nu_3$ mode van $SF_6$ te beschrijven en te bepalen, moeten veel meetgegevens verzameld worden Een probleem hierbij is dat de $CO_2$ lasers of zeer slechte bundeleigenschappen hebben (gepulste lasers), óf maar een klein deel van het te meten gebied bestrijken (continue lasers) In dit proefschrift worden twee manieren gepresenteerd om het te meten frequentiegebied uit te breiden Ten eerste zijn acousto optic modulators (AOM's) gebruikt, in deze kristallen wordt de frequentie van de laserstraling +100 MHz of -100 MHz verschoven De AOM kan voor een tweede keer gekruist worden, waardoor er een +200 MHz of -200 MHz shift ontstaat Het frequentie gebied van de laser kan op deze manier verdubbeld worden De metingen, verricht met deze

experimentele set-up, zijn beschreven in hoofdstuk 2 van dit proefschrift De toekenning van de twee-fotonovergangen is gedaan in samenwerking met Sartakov (Moscow) en Pierre (Dijon), de resultaten zijn weergegeven in hoofdstuk 3

Om het te bereiken frequentiegebied nog wat uit te breiden is een experimentele truc toegepast Twee $CO_2$ waveguide-lasers worden precies op de moleculaire bundel gekruist Twee-fotonovergangen, geproduceerd met twee fotonen ieder van een andere laser, kunnen nu gemeten worden Door verschillende combinaties van laserlijnen te kiezen zijn 95 nieuwe twee-fotonovergangen gemeten en toegekend De experimentele gegevens, alsmede enkele metingen, zijn besproken in hoofdstuk 4 In hoofdstuk 5 worden de meetresultaten gepresenteerd en besproken

Niet alleen twee-fotonovergangen zijn gemeten, er is ook een begin gemaakt met de spectroscopie van de drie- en vier-fotonovergangen Enkele toegekende lijnen zijn gegeven in hoofdstuk 5

Naast de spectroscopie, die de hoofdmoot vormt van dit proefschrift, zijn nog enkele andere interesante effecten bestudeerd Ten eerste het rapid adiabatic passage proces, waarmee het mogelijk is de moleculen voor 100% in de aangeslagen toestand te krijgen Door middel van een juiste keuze van de lenzen die gebruikt worden om de $CO_2$ lasers te focusseren op de moleculaire bundel kan RAP verwezenlijkt worden Dat we er ook in geslaagd zijn deze condities te verwezenlijken is bewezen in hoofdstuk 2, waar door middel van probing van het aangeslagen niveau, in een dubbelresonantie-experiment een negatief bolometersignaal waargenomen is Dit is alleen mogelijk als er populatie-inversie veroorzaakt is bij de eerste laserinteraktie Een andere indicatie voor het feit dat we in onze experimenten onder RAP condities meten, is de afwezigheid van vermogensverbreding en Rabi-oscillaties In conventionele spectroscopie worden lijnbreedtes van meer dan 100 MHz verwacht bij de vermogens die wij gebruiken (typisch in de orde van grootte van 10 Watt, dit is 1000 keer het vermogen nodig om een één-fotonovergang te verzadigen), wij meten een FWHM van 2 MHz

Dat het ook mogelijk is onder niet-RAP condities te werken is bewezen in hetzelfde hoofdstuk Voor het eerst is een twee-foton Rabi-oscillatie gemeten

In een aanzet om het quasicontinuum te onderzoeken is gekeken naar welke energieniveaus er een rol spelen in het multifotonproces waarbij met een sterke laser in één keer vijf fotonen in het molecuul gestopt worden Het blijkt dat vooral de moleculen die zich al in een aangeslagen toestand bevinden (hot bands) meedoen in dit proces Moleculen die starten vanuit de grondtoestand spelen een ondergeschikte rol

Een overzicht van onderzoeken die gedaan kunnen worden gebruik makende van de kennis vergaard in dit proefschrift is gegeven in hoofdstuk 6, de outlook

# Curriculum Vitae

**Sacco te Lintel Hekkert**

| | |
|---|---|
| Geboren | 11 maart 1963 |
| Geboorteplaats | Deventer |
| 1975–1979 | MAVO, Gemeentelijke Scholen Gemeenschap Doetinchem |
| 1979–1981 | HAVO, Gemeentelijke Scholen Gemeenschap Doetinchem |
| 1981 1983 | VWO, Gemeentelijke Scholen Gemeenschap Doetinchem |
| 1983–1988 | Studie natuurkunde aan de Katholieke Universiteit Nijmegen, afgestudeerd bij de experimentele afdeling Molecuul- en Laserfysica van prof dr J Reuss |
| 1987–1988 | Onderzoek naar de mogelijkheden om het frequentiebereik van een gepulste YAG-laser te vergroten met behulp van een Raman-shifter, een heatpipe en niet-lineaire kristallen, tevens metingen verricht aan het foto akoestische effect van kool-waterstofverbindingen opgelost in tetra (afstudeerproject) |
| 1988 | Bouw dubbele $CO_2$ intra-cavity laser in dienst van de afdeling Molecuul- en Laserfysica |
| 1989 | Bij het onderzoekscentrum ENEA, Frascati (Italie) onderzoek verricht naar het multifotonproces in $SF_6$ met behulp van een gepulste continu verstembare hogedruk $CO_2$ laser |
| 1989–1993 | Promotie-onderzoek op de afdeling Molecuul- en Laserfysica met prof dr J Reuss als promotor Resultaten van het onderzoek zijn weergegeven in dit proefschrift In het kader van de onderwijsbegeleiding werd een half jaar assistentie verleend bij het practicum voor scheikunde studenten en anderhalf jaar begeleiding gegeven aan studenten bij het basiscolloquium, een algemeen vormend colloquium |
| januari 1991 | Op het Max-Planck instituut te Gottingen botsingen tussen Na-atomen en aangeslagen $SF_6$ moleculen onderzocht |
| juli 1992 | Universiteit in Dijon bezocht om te helpen de in Nijmegen verkregen meetresultaten theoretisch te onderbouwen |